

THE ION-EXCHANGE REACTIONS OF RADIOACTIVE
IONS WITH SOILS AND EFFECTS OF ORGANIC COMPOUNDS

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Final Report
Project A-004-ILL

Supported by
University of Illinois
Water Resources Center
with funds from
Office of Water Resources Research
U.S. Dept. of the Interior
Agreement No. 14-01-0001-907

Department of Civil Engineering
University of Illinois
Urbana, Illinois
October 1966

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University of Illinois, 1966

The ion-exchange reactions of radionuclides with soil minerals and the effects of various water-soluble organic compounds on the reactions were investigated.

Various theories concerned with ion-exchange reactions were examined for their practicability in predicting the equilibrium distribution of radionuclides in a soil environment. The effects of various water-soluble organic compounds on the ion-exchange reactions of a radionuclide with soil minerals (Mississippi montmorillonite and Fithian Illite) were studied using organic compounds selected from the groups which are known to be present in the natural environment and in certain wastes discharged from nuclear facilities. The organic compounds include those which interact with metal ions (both the radionuclides and the competing counter ions) and others which may interact with soil particle surfaces. The effects of the interactions of organic compounds with counter ions were examined using chelating agents, citrate, tartrate, and EDTA. Several soil-sorptive organic compounds (methylamine, dodecylamine, methylene blue, and arginine) were used to determine the effects of organic adsorption on the ion-exchange properties of soil minerals. Organic compounds extracted from ground water and surface soils were also used to investigate the effects of these extracts and to compare the

results with those of the pure organic compounds used.

Experimental results indicate that the mass-action law can be applied to describe ion-exchange equilibria in most systems except those involving hydrogen ions. Difficulties of applying theories for a system involving hydrogen ions resulted from the fact that the ion-exchange sites of the clay minerals consisted of different types of sites. General rules of selectivity hold for most pairs of counter ions regardless of the types of exchange sites; however, due to different types of reactions involved, the selectivity of hydrogen changed as the ions occupied the exchange sites.

In the study of the effects of chelating agents, an effort was made to examine the theories concerned with ion exchange and metal chelate chemistry as they apply to predicting the distribution of radionuclides in a system containing soils, chelating agents, and several competing counter ions. The effects of chelating agents on the distribution of strontium ions in equilibrium with soil ion-exchange media followed the general rules regarding the stability of metal chelates and the selectivity of soil exchange media. The effects depended on the nature and the concentration of the competing counter ion present. In the presence of counter ions (Ca^{++} and Zn^{++}) that formed more stable chelates than Sr^{++} , the presence of chelating agents increased the exchange adsorption of Sr^{++} ions on soil exchange media; on the other hand, when the counter ions (Mg^{++} and Na^{+}) that formed less stable chelates were present, chelating agents increased the concentration of Sr^{++} ions in the solution phase.

The effects of organic adsorption were examined in terms of changes in the soil ion-exchange parameters such as the exchange

capacities and the selectivity of soil exchange media. The experimental results indicated that certain organic compounds were irreversibly adsorbed on soil particle surfaces and had considerable effects on their ion-exchange parameters. Irreversible adsorption of organic compounds not only reduced the effective exchange capacities, but also changed the selective properties of the exchange media. In general, the selectivity for a cation in preference to others increased as soil particle surfaces were covered with organic compounds.

The experimental results with natural organic extracts indicated that the effects of the extracts were similar to those of weak chelating agents. The degree of the effects was somewhat less than that of pure chelating agents used. As a result of the inefficient method of extraction used, the extracts are believed to contain only a small fraction of the natural organic compounds present in the original sample.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to all those whose assistance helped in bringing this work to successful completion. The author is indebted to his advisor, Professor Ben B. Ewing, for his guiding assistance in the research and the writing of this thesis. Special acknowledgements are also extended to Dr. Richard Engelbrecht and Dr. Marvin Wyman and all the personnel in the Sanitary Engineering Laboratory who have helped to make this work possible. The work upon which this publication is based was supported in part by funds provided by the United States Department of the Interior as authorized under the Water Resources Research Act of 1964, Public Law 88-379.

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1. INTRODUCTION

Radioactive contaminants created by nuclear processing plants or by bomb tests may enter the soil environment as fallout materials, as low-level wastes being disposed into the environment, or as a result of accidents whereby storage facilities or processing plants release them. As the magnitude of the nuclear industry grows, the problems of nuclear waste treatment and contamination of the environment with radioactive waste are inevitable.

Transport of these radionuclides through soil media is a consequence of the movement of transporting water, but they are also retained by adsorptive properties of the soil media. The role of natural soil media in retaining or transporting radionuclides is becoming increasingly important. In the interest of water supply and food production from soils, greater care and precision will be required to evaluate the fate of radionuclides in the soil environment.

It is a well established fact that the ion-exchange properties of soil materials play important roles in retaining or transporting the radionuclides released into a soil environment. Ion-exchange reactions of hazardous radionuclides such as Sr^{90} and Cs^{137} with soil and its clay fraction have been studied by many investigators⁽¹⁾ not only for the purpose of investigating the fate of the radionuclides, but also for the treatment of radioactive waste by exchange adsorption.

Equilibrium distribution of radionuclides released into the soil environment are controlled by various chemical and physical conditions of the environment. Of many possible factors which may govern the ion-exchange reactions of soil materials, the presence of various inorganic

salts, the pH of the environment, and properties of clay fraction of soil materials are important and have been studied for their effects.

Various theories involved in ion-exchange reactions of soil materials have been developed. Within the frame of conditions assumed for their development, the theories are satisfactory; however, universal application of these theories for actual soil environments is limited because of the complexity of over-all reactions involved in the natural soil environment.

In order to be able to predict more accurately the equilibrium distribution of radionuclides disposed into the soil environment, further study of the fundamental mechanisms of soil ion exchange and other possible factors which may affect the ion-exchange reactions of soil media is needed.

One of the areas in which further investigation is needed for a better understanding of soil ion-exchange reaction is the effects of water-soluble organic compounds present in the system. It is a known fact that natural water⁽²⁾ and certain wastes discharged from nuclear facilities contain many types of dissolved organic compounds. Furthermore, natural soils contain humus type organic compounds which are either the degradation products of vegetable matter or the products of microbial synthesis. Stevenson and his co-workers⁽³⁾ have shown the presence of various amino acids adsorbed on soil particles. Though considerable research work has been conducted with regard to ion-exchange reactions between radionuclides and soil exchange media, these studies were generally performed with ideally simplified systems containing soils and distilled water solutions in the absence of any organic compounds. The interactions of individual organic constituents in a natural soil environment and their effects on the ion-exchange properties of the soil environment have not been studied.

To have a better understanding of what happens to radionuclides when they enter the natural soil environment, a knowledge of over-all reactions including the interactions of the organic compounds with soil constituents and their effects on the ion-exchange reaction is needed.

1.1. Purpose and Scope of the Investigation

There now exists a large amount of data on ion-exchange properties of soil materials. In general, these data have been obtained from ideally simplified systems. These data alone are inadequate for the prediction of the actual equilibrium distribution of radionuclides released into a soil environment, for in a natural soil environment various other interactions may affect the ion-exchange reactions. One such area in which further investigation is needed is the effect of dissolved organic compounds.

It has been shown that in a natural soil environment there are present various organic compounds⁽²⁾ which may interact with both competing counter ions and the soil exchange media. Some of the organic compounds present in natural water are believed to be multi-hydroxy-carboxylic compounds which may readily interact with metal ions present in the system. The extraction of proteins and amino-acid-type organic compounds⁽³⁾ from natural soil materials indicates the presence of soil-sorptive organic compounds in the natural soil environment. Recently, ORNL⁽⁴⁾ and NRTS⁽⁵⁾ in their investigations of ion-exchange properties of radioactive wastes with soil media included the study of the effects of various complexing agents present in their wastes.

It is the purpose of this investigation to study the mechanism

of soil ion exchange and the effects of various organic compounds. Organic compounds selected for the investigation were chelating agents, a polar compound, organic cations, and organic extracts from natural water and surface soil materials. On the basis of their interaction, these organic compounds are grouped into two categories, one which interacts with counter ions and the other which interacts with soil particle surfaces.

To examine the mechanism of soil ion exchange and the applicability of present theories, ion-exchange reactions of various counter ions with soil minerals (montmorillonite and illite) were first studied in the absence of organic compounds. The studies included the determination of soil ion-exchange parameters and the applicability of data obtained from simple systems to more complex systems.

The interactions of counter ions (Na^+ , Ca^{++} , Mg^{++} , and Sr^{++}) with chelating agents and their effects on ion-exchange reactions were studied by batch equilibrium-type experiments with tartrate, citrate, and EDTA. The laboratory findings were examined in terms of existing theories concerning ion exchange and metal chelate chemistry.

Several organic compounds having cationic properties (methylamine, methylene blue, dodecylamine, and arginine) were used to study adsorption and its effects on the ion-exchange properties of soil minerals. The relative selectivity of soil minerals for the organic cations with respect to inorganic counter ions (Na^+ and Sr^{++}) was determined. The effects of adsorbed organic compounds on the ion-exchange properties of soil minerals were examined in terms of changes in the exchange parameters.

In order to compare the effects of various pure organic compounds with those of organic compounds present in the natural environment, organics extracted from ground water and surface soils were also used in the investigation. The effects of the extracts were examined in terms of changes in distributions of counter ions in the presence of the extracts.

2. THEORY AND MECHANISM OF ION EXCHANGE

2.1. Theory of the Ion-Exchange Phenomena

The various explanations that have been proposed for the ion-exchange phenomena have been widely divergent. These explanations may be grouped into three theories⁽⁶⁾: (1) the double-layer theory, (2) the Donnon membrane theory, and (3) the crystal lattice exchange theory.

2.1.1. The Double-Layer Theory

The double-layer theory⁽⁷⁾, developed as an explanation of the electrokinetic properties of colloids, has been considered as an explanation for the various phenomena associated with ion exchange. The double-layer model of charged colloids consists of an inner fixed layer with a diffuse and mobile outer layer of charges. The ions present in the diffuse outer layer of a colloid extend into the external liquid medium. It may be considered that the concentration of the ions constituting the diffuse outer layer is varying continuously and depends on the concentration and pH of the external solution. If the concentration of the ions in the external solution is changed by addition of a foreign ion, the equilibrium is upset and a new equilibrium is obtained. Some new ions will enter the diffuse outer layer, exchanging the ions previously held in this layer. The capacity of the diffuse outer layer depends on the concentration and pH of the external solution.

2.1.2. The Donnon Membrane Theory

A special case of the Donnon membrane theory^(8, 9) has been

applied to explain the ion-exchange phenomena occurring in various exchange media. The Donnon membrane theory pertains to the unequal distribution of ions on two sides of a semipermeable membrane, one side containing an electrolyte, one of whose ions is not able to diffuse through the membrane. Bauman and Eichhorn⁽¹⁰⁾, applying a Donnon membrane equilibrium approach, considered an ion-exchange medium as a very concentrated solution of functional groups separated from the surrounding solution by a semipermeable membrane. The functional groups (exchange media) are considered as the non-diffusible ions.

For the solution containing electrolyte AX, the chemical potential of electrolyte AX at equilibrium must be the same at both sides of the membrane.

$$\bar{U}_{AX} = \bar{U}_{AX}^{\circ} + R T \ln \bar{a}_{AX}$$

$$\bar{U}_{AX} = U_{AX} = U_{AX}^{\circ} + R T \ln a_{AX}, \quad (2-1)$$

where \bar{a}_{AX} and a_{AX} refer to the activities of the electrolyte AX in the exchanger and solution phases, respectively.

In the first approximation, the standard chemical potentials (\bar{U}_{AX}° and U_{AX}°) of the electrolyte AX are considered as being equal on both sides, so that at constant temperature Equation (2-1) may be reduced to

$$\bar{a}_{AX} = a_{AX}, \quad (2-2)$$

which can be written in the form,

$$\bar{a}_A \bar{a}_X = a_A a_X \quad (2-3)$$

Equation (2-3) shows the fact that in the exchange medium with high exchange capacity ($\bar{a}_A > a_A$) the invasion of negative ion, X, is small. For the system containing the ion exchanger in ionic form B, and surrounded by the solution with another electrolyte BX, the ionic distribution of electrolyte, BX, follows the same rule as AX.

$$\bar{a}_B \bar{a}_X = a_B a_X \quad (2-4)$$

After eliminating the anion, X, which is common to both cations, A and B, the relationship of the cation A to cation B is,

$$\frac{\bar{a}_A}{\bar{a}_B} = \frac{a_A}{a_B}$$

For a pair of ions of unequal valence, such as Na^+ and Ca^{++} , the relationship is

$$(\bar{a}_{\text{Ca}}) (\bar{a}_X)^2 = (a_{\text{Ca}}) (a_X)^2$$

and

$$(\bar{a}_{\text{Na}}) (\bar{a}_X) = (a_{\text{Na}}) (a_X) \quad (2-5)$$

After eliminating the anion, X, the relationship becomes,

$$\frac{(\bar{a}_{\text{Na}})^2}{(\bar{a}_{\text{Ca}})} = \frac{(a_{\text{Na}})^2}{(a_{\text{Ca}})} \quad (2-6)$$

These relationships simply state that the exchange of ions must take place until the activity ratios are equal in both phases. The accuracy of the Donnon membrane theory for the description of an ion-exchange equilibrium is questionable because it does not consider any of the physical forces involved in the ion-exchange process; however, the Donnon concept clearly explains the inability of free electrolyte to enter the exchanger phase, the effect of valence, and the effects of concentrations.

2.1.3. The Crystal Lattice Theory

The concept of the nature of ionic solids has been applied to silicate minerals exhibiting the ion-exchange phenomena. An ion at the surface of a crystal is subject to less attractive forces than a similar ion beneath the crystal surface. If placed in a highly polar medium such as water, the net attractive forces binding the surface ion to the crystal are diminished to such a degree that the exchange of this ion is possible. The exchangeability of the surface ions depends on the nature of the binding force, the ion's charge, concentration, size, solubility, as well as its accessibility to the surface.

The exchange of ions in silicate minerals^(11, 12) such as zeolite and clay minerals is quite similar to that of the crystal lattice ions. The exchangeable cations on silicate minerals are there to balance the positive charge deficiency created by the imperfect crystallinity of these silicate minerals. Nonetheless these exchangeable cations on silicate minerals occupy essential lattice sites.

All the ion-exchange theories are quite similar in that the exchange of ions must satisfy the law of electroneutrality. The differences are the position and the origin of the exchange sites. The crystal lattice exchange theory assumes a fixed number of exchange sites that must be satisfied regardless of changes in the concentration or the pH of the external solution. However, in the double-layer theory this is not true since the diffuse outer layer depends on both concentration and pH. In a certain system both types of exchange may occur simultaneously, the quantity depending on the nature of the exchange medium. The Donnan membrane theory does not conflict with either the crystal lattice theory or the double-layer theory, but merely offers a quantitative relationship for an exchange process.

2.1.4. The Ion-Exchange Theory of Soils

Numerous experimental results indicate that the ion-exchange properties of soils depend on the activities of the clay fraction. Both the crystalline structure and the micro-size of clay minerals contribute to the magnitude of the ion-exchange properties. Grim⁽¹³⁾ cites three causes of the cation exchange properties: (1) broken bonds, (2) lattice substitution, and (3) replacement of hydrogen from exposed hydroxyl groups.

Broken bonds around the edge of silicate alumina units give rise to unsatisfied charges, which are balanced by adsorbed cations. The number of broken bonds is increased by breaking the particle into smaller pieces; hence, the exchange capacity is increased as the particle size decreases. In illite, chlorite, kaolinite, and holloysite minerals,

broken bonds are the major contributor to the exchange capacity.

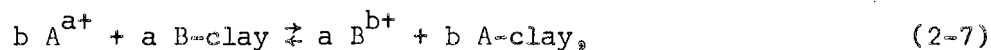
Substitution of aluminum for silicon in the tetrahedral sheet and substitution of lower valence cations, particularly magnesium, for trivalent aluminum in the octahedral sheet result in unbalanced positive charge deficiencies, which are balanced by adsorbed cations. In montmorillonite and vermiculite, substitution within the lattice structure gives rise to the major portion of their exchange capacities.

The hydrogen of exposed hydroxyl groups in the basal cleavage or around the broken edge of clay minerals may be exchangeable by other cations. This type of exchange site may be sensitive to environmental conditions, particularly the pH of the solution.

2.2. Ion-Exchange Equilibrium and Terminology

Ion-exchange equilibrium is attained when an ion exchanger is placed in an electrolyte solution containing a counter ion (A^{a+}) which is different from that (B^{b+}) in the exchanger. At equilibrium, both the exchanger and the solution contain both competing counter ions, A^{a+} and B^{b+} . The ion exchange reaction is, as a rule, reversible. Thus it makes no difference from which side equilibrium is approached; that is whether A^{a+} is exchanged for B^{b+} or B^{b+} for A^{a+} .

For the description of an ion-exchange equilibrium in which a moles of counter ion B^{b+} are being exchanged by b moles of counter ion A^{a+} ,



$$Kd_A = \frac{\bar{m}_A}{m_A}$$

In terms of the distribution coefficients, the selectivity coefficients can be expressed as

$$Ko_{AB} = \frac{Kd_A}{Kd_B}$$

The mass-action equilibrium constant, Ko'_{AB}

For the ion-exchange reaction, which is governed by the law of mass-action, the equilibrium condition is often described in terms of the mass-action equilibrium constant,

$$Ko'_{AB} = \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{a_B}{\bar{a}_B} \right)^a \quad (2-9)$$

where \bar{a}_A , \bar{a}_B and a_A , a_B are the activities of the counter ions, A^{a+} and B^{b+} , in the exchanger and solution phases, respectively. The mass-action equilibrium constant and the selectivity coefficient are interrelated by

$$Ko'_{AB} = Ko_{AB} \left(\frac{\bar{\gamma}_A}{\gamma_A} \right)^b \left(\frac{\gamma_B}{\bar{\gamma}_B} \right)^a \quad (2-10)$$

where $\bar{\gamma}_A$ and γ_A represent activity coefficients of the ion A^{a+} in the exchanger and solution phases, respectively.

It is important to note that the mass-action equilibrium constant, Ko'_{AB} , applies to the system only if the ion-exchange reaction is governed by the law of mass-action. As will be discussed in a later section, the exchange reactions of montmorillonite and illite used in

this investigation do indeed follow the law of mass-action.

The thermodynamic equilibrium constant, K_{thAB}

In theoretical studies thermodynamic equilibrium constants are often used, which represent true thermodynamic characteristics of the ion-exchange reaction and have truly constant values depending only on temperature. This quantity is defined by the thermodynamic relation,

$$\Delta G^{\circ} = - R T \ln K_{th}$$

where ΔG° is the standard free energy change of the ion-exchange reaction which includes the exchange of counter ion B^{b+} by A^{a+} , and the sorption and desorption of solvents and electrolytes.

2.3. Evaluation of Ion-Exchange Equilibrium

For the ion-exchange reaction in which the exchange of a moles of counter ion B^{b+} by b moles of counter ion A^{a+} is accompanied by desorption of f moles of electrolyte BX and sorption of g moles of electrolyte AX and h moles of the solvent, the free-energy change of the total system⁽¹⁴⁾ is,

$$\begin{aligned} \Delta G = \Delta G^{\circ} + R T \ln \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{a_B}{\bar{a}_B} \right)^a - R T \left(\frac{\bar{a}_{BX}}{a_{BX}} \right)^f \\ + R T \ln \left(\frac{\bar{a}_{AX}}{a_{AX}} \right)^g + R T \ln \left(\frac{\bar{a}_w}{a_w} \right)^h \end{aligned} \quad (2-11)$$

At equilibrium the total free energy change becomes zero. Thus Equation (2-11) becomes,

$$\begin{aligned}\Delta G^{\circ} &= - R T \ln K_{th_{AB}} \\ &= - R T \ln \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{a_B}{\bar{a}_B} \right)^a + R T \left(\frac{\bar{a}_{BX}}{a_{BX}} \right)^f - \ln \left(\frac{\bar{a}_{AX}}{a_{AX}} \right)^g \\ &\quad - R T \ln \left(\frac{\bar{a}_w}{a_w} \right)^h, \quad (2-12)\end{aligned}$$

and

$$K_{th_{AB}} = \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{a_B}{\bar{a}_B} \right)^a \left(\frac{a_{BX}}{\bar{a}_{BX}} \right)^f \left(\frac{\bar{a}_{AX}}{a_{AX}} \right)^g \left(\frac{\bar{a}_w}{a_w} \right)^h \quad (2-13)$$

Equation (2-11) contains only thermodynamically defined quantities and represents the true equilibrium reaction. It reflects all the possible effects of the various factors which may be accompanying the exchange of the counter ion B^{b+} by A^{a+} . If the sorption of electrolyte and changes in swelling resulting from the adsorption of the solvent can be neglected, the thermodynamic equilibrium constant is reduced to the mass-action equilibrium expression,

$$K_{th_{AB}} = \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{a_B}{\bar{a}_B} \right)^a$$

For many years, ion-exchange equilibria have been the subject of numerous experimental and theoretical investigations. The most

appropriate means of describing an ion-exchange equilibrium is by thermodynamics. Many investigators have attempted to describe an ion-exchange equilibrium by thermodynamic treatment^(15, 16); however, the practical application of such a treatment is restricted because the quantities involved can not be determined by independent measurement nor can they be predicted without using non-thermodynamic assumptions. Though the rigorous thermodynamic treatment is correct and universal, it yields little information about the actual physical causes of the ion-exchange phenomena to which the treatment is applied. Therefore, models with particular properties resembling those of the exchanger have been introduced for deriving equations that reflect the action of the various physical forces. With such models the effects of particular properties of an exchanger can be analyzed. However, every commitment of a model with particular properties means a deviation from rigorous thermodynamics, and equations developed from the model can only be applied to a system with identical properties. Furthermore, ion-exchange reactions of an exchanger depend on a variety of forces, which makes any theoretical treatment using a model with all the physical forces unmanageably complex.

Even though none of the theoretical treatments of an ion-exchange process derived from a model have been satisfactory for practical application, it is of interest to examine the effects of particular properties of an ion-exchanger on the behavior of the system. The first model that reflects any of the particular properties of an ion-exchanger was introduced by Gregor⁽¹⁷⁾. According to his model, an ion exchanger is a network of elastic springs. When the exchanger swells, the network is stretched and exerts a pressure on the internal pore, and the swelling

pressure in the exchanger affects the ion-exchange equilibrium. Gregor, from his elastic spring model of an ion exchanger, derived the relation,

$$\begin{aligned}
 K_{th_{AB}} &= R T \ln \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{a_B}{\bar{a}_B} \right)^a \\
 &= \pi (a v_B - b v_A) \quad (2-14)
 \end{aligned}$$

where π is swelling pressure and v_A , v_B are partial molar volumes of the counter ion A^{a+} and B^{b+} .

The practical application of Equation (2-14) is restricted by difficulties of evaluating the activity coefficients, π , v_A , and v_B . Qualitatively Gregor's model and his equation explain the selectivity sequence of the alkali ions ($Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$), which is in the same sequence as that of decreasing hydrated volume.

Pauley⁽¹⁸⁾ has interpreted the selectivity of an ion exchanger in terms of a simple model, whose essential feature is the electrostatic attraction between the counter ions and the fixed ionic sites of the exchanger. Assuming that all the counter ions in the exchanger are found at their distance of closest approach to the fixed ionic sites of the exchanger, from Coulomb's law the ion-exchange equilibrium constant for univalent counter ions is expressed as,

$$\ln K_{th_{AB}} = q \left(\frac{1}{d_B^O} - \frac{1}{d_A^O} \right), \quad (2-15)$$

where d_A^O and d_B^O are the distance of closest approach between the counter ions and the fixed ionic sites of the exchanger.

According to Equation (2-15), the counter ion with the smaller d^0 value is preferred. Pauley's equation explains the selectivity series of alkali ions ($\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$), which is the same as the series of the Debye-Huckel parameter, d^0 , for the alkali ions. There is no doubt but that the situations in actual systems are much more complicated by interactions other than simple electrostatic reactions.

2.3.1. The Mass-Action Expression of Ion-Exchange Reactions

Many theoretical approaches and models have been developed and used for the description of the equilibria existing between ion-exchangers and electrolyte solutions; however, a universally applicable solution does not exist. In all cases, one uses either a selectivity coefficient or a mass-action equilibrium constant, both of which may be corrected somewhat to give an acceptable equilibrium constant.

The reversibility of the ion-exchange process, coupled with the equivalence of the exchange, has indicated the possibility of applying the law of mass-action, particularly for the exchangers with rigid structures, such as zeolites and clay minerals, both of which display negligible changes in adsorption of solvents and electrolytes. The mass-action equilibrium constant for the reaction where \underline{b} moles of the counter ion A^{a+} is replacing \underline{a} moles of the counter ion B^{b+} may be written in the form of,

$$\begin{aligned}
K_{O_{AB}} &= \left(\frac{\bar{a}_A}{a_A} \right)^b \left(\frac{\bar{a}_B}{a_B} \right)^a \\
&= \left(\frac{\bar{m}_A}{m_A} \right)^b \left(\frac{\bar{m}_B}{m_B} \right)^a \left(\frac{\bar{\gamma}_A}{\gamma_A} \right)^b \left(\frac{\bar{\gamma}_B}{\gamma_B} \right)^a \\
&= K_{O_{AB}} \frac{(\gamma_B)^a}{(\gamma_A)^b} \frac{(\bar{\gamma}_A)^b}{(\bar{\gamma}_B)^a}
\end{aligned} \tag{2-16}$$

Investigators generally agree that the solution phase activity correction factor may be approximated by,

$$\frac{(\gamma_B)^a}{(\gamma_A)^b} = \frac{(\gamma_{\pm BX})^{(zb+1)a}}{(\gamma_{\pm AX})^{(za+1)b}} \tag{2-17}$$

where $\gamma_{\pm AX}$ and $\gamma_{\pm BX}$ are the mean activity coefficients of electrolytes AX and BX, and za and zb are the valences of the counter ions, A^{a+} and B^{b+} . The mean activity coefficient of a pure electrolyte can be calculated from the Debye-Huckel expression,

$$\ln \gamma_{\pm} = \frac{-A (Z_+ Z_-) \sqrt{I}}{1 + BXd \sqrt{I}} \tag{2-18a}$$

$$\text{with the ionic strength, } I = 1/2 \sum m_i Z_i^2 \tag{2-18b}$$

$$A = \frac{1.8246 \times 10^6}{(DT)^{3/2}}, \quad B = \frac{50.29 \times 10^8}{(DT)^{1/2}}$$

where D is the dielectric constant and T the absolute temperature.

For most practical purposes Equation (2-18a) can be approximated⁽¹⁹⁾ by,

$$\ln \gamma_{\pm} = - \frac{0.511 (Z_+ Z_-) \sqrt{I}}{1 + 0.329 \times 4.0 \sqrt{I}} \quad (2-19)$$

where the average effective diameters of counter ions are taken to be 4.0 \AA , and constants are evaluated at the temperature of 25°C .

Since an ion-exchange reaction always involves more than one electrolyte, the mean activity coefficients must be for a mixed electrolyte; however, there being a lack of means for determining the activity coefficients of mixed electrolytes, certain approximations are necessary. In this investigation, the mean activity coefficients of mixed electrolytes, $A_x X_a$ and $B_y Y_b$, are computed under two assumed conditions: (a) the activity coefficients of the two cations do not show mutual interference and the values of the coefficient are the same as those for either of the pure, individual electrolytes; (b) the activity coefficients do not show mutual interference, but the values are the same as those of the pure electrolytes having the total electrolyte concentrations. The difference in the two assumptions is in the value of the ionic strength, and the actual values of the activity coefficients will lie between these two values. Under the second assumption, the activity coefficients of the counter ions of the same valence in the same solution are identical, and the ratio of the activity coefficients becomes unity.

There have been many attempts to evaluate the activities of the exchanger phase, correlating the activities with the quantities that are accessible by independent measurement. However, there is no general agreement concerning the activities of the exchanger phase. The first approach to evaluating these activities was given by Vansellow⁽²⁰⁾, who considered the exchanger phase as a completely miscible, ideal mixture,

and the activity of each component as being equal to its mole fraction in the exchanger. With this assumption employed, the activity ratio of counter ions in the exchanger phase is,

$$\frac{(\bar{a}_A)^b}{(\bar{a}_B)^a} = \frac{\left(\frac{\bar{C}_A}{\bar{C}_A + \bar{C}_B}\right)^b}{\left(\frac{\bar{C}_B}{\bar{C}_A + \bar{C}_B}\right)^a} \quad (2-20a)$$

and the ratio of the activity coefficients becomes,

$$\frac{(\bar{\gamma}_A)^b}{(\bar{\gamma}_B)^a} = \left(\frac{\bar{m}_A}{z_a} + \frac{\bar{m}_B}{z_b}\right)^{a-b}, \quad (2-20b)$$

where \bar{C}_A and \bar{C}_B are the molar concentration of the counter ions, A^{a+} and B^{b+} , and \bar{m}_A and \bar{m}_B are the normal concentrations.

Davis⁽²¹⁾, and Krishnamoorthy and Overstreet⁽²²⁾, applying statistical thermodynamics, derived a semi-empirical formula for the activities of counter ions, A^{a+} and B^{b+} , in the exchanger phase. For an exchanger containing counter ions A^{a+} , B^{b+} , C^{c+} , and D^{d+} , the activity ratio of the counter ions, A^{a+} and B^{b+} , is,

$$\frac{(\bar{a}_A)^b}{(\bar{a}_B)^a} = \frac{(\bar{C}_A)^b}{(\bar{C}_B)^a} \times (q_a \bar{C}_A + q_b \bar{C}_B + q_c \bar{C}_C + q_d \bar{C}_D)^{a-b} \quad (2-21a)$$

and the ratio of activity coefficients becomes

$$\frac{(\bar{Y}_A)^b}{(\bar{Y}_B)^a} = (q_a \frac{\bar{m}_A}{z_a} + q_b \frac{\bar{m}_B}{z_b} + q_c \frac{\bar{m}_C}{z_c} + q_d \frac{\bar{m}_D}{z_d})^{a-b}, \quad (2-21b)$$

where $q_i = \frac{z_i+1}{2}$, and z_i = the valence of the counter ion, I^{i+} .

Krishnamoorthy and Overstreet^(23, 24) have found this relationship to fit the ion-exchange equilibrium data of clay exchange systems for all ion pairs except those involving hydrogen ions.

The mass-action equilibrium expression has been found quite satisfactory for most counter ion pairs. However, there are a few exceptions where the mass-action equilibrium expression does not describe the distribution of counter ions in equilibrium with clay mineral exchangers. It has been shown that cations such as potassium ions⁽²⁵⁾ are sometimes fixed on the clay minerals after being adsorbed by the ion-exchange process. Under this condition the ion-exchange process will be irreversible, and the mass-action law will not be valid. Soils are composed of many different constituents, which may be quite different in their ion-exchange properties. The equilibrium constant derived from the mass-action law may not be a constant value for such a mixture but may depend on the conditions imposed on the system.

2.4. Ion-Exchange Reactions of Heterogeneous Clay Mixtures

The ion-exchange equations that have been discussed in the previous section are only applicable to mineralogically pure samples of clays in which all exchange sites are identical in their properties. Theoretically, if the equilibrium constant for a given ion pair is K_x for a pure exchanger X, and K_y for a pure exchanger Y, then in a mixture of

exchanger X and Y, no satisfactory equilibrium constant⁽²⁶⁾ can be found for the ion pair. For example, for the ion-exchange reaction of the counter ions, Sr^{++} and Mg^{++} , with a mixture of montmorillonite and illite, if the effective equilibrium constant of the mixture is defined as,

$$\overline{K}_{\text{Sr-Mg}} = \frac{\overline{m}_{\text{Sr}} \overline{m}_{\text{Mg}}}{\overline{m}_{\text{Sr}} \overline{m}_{\text{Mg}}}, \quad (2-22)$$

then it can be shown that the effective equilibrium constant in terms of the ion-exchange parameters of montmorillonite and illite is,

$$\overline{K}_{\text{SrMg}} = \frac{(C.E.C.)_m + (C.E.C.)_i + \left[\frac{(C.E.C.)_m}{(K_{\text{SrMg}})_i} + \frac{(C.E.C.)_i}{(K_{\text{SrMg}})_m} \right] \times \frac{m_{\text{Mg}}}{m_{\text{Sr}}}}{(C.E.C.)_m + (C.E.C.)_i + \left[\frac{(C.E.C.)_m}{(K_{\text{SrMg}})_m} + \frac{(C.E.C.)_i}{(K_{\text{SrMg}})_i} \right] \times \frac{m_{\text{Mg}}}{m_{\text{Sr}}}}, \quad (2-23)$$

where the subscripts, m and i, refer to the montmorillonite and illite, and C.E.C. to the cation exchange capacity.

Equation (2-23) shows the dependency of the effective equilibrium constant on the mixing of clays and the concentration of the counter ions. Thus, a soil that contains a mixture of minerals with different properties may not give a satisfactory equilibrium constant. If the equilibrium constants of two pure minerals are the same, the effective equilibrium constant of the mixture of these clay minerals reduces to the same value as that for the pure clay minerals. If the equilibrium constants of pure minerals do not differ greatly, then the effect of mixing will not be great.

2.5. Ion-Exchange Equilibrium in a Multicomponent System

In practical application, ion-exchangers are usually exposed to more than two counter ions. The rules for the selectivity of an ion exchanger are essentially valid also in the system with more than two counter ions. If the presence of a third cation does not affect the equilibrium between any two given cations except by competing itself for the exchange sites, then the competition of the various cations for the exchange sites can be expressed by independent equilibrium reactions. In this event, the system must meet the conditions imposed by a number of simultaneous equilibria. Krishnamoorthy and Overstreet⁽²³⁾ reported that for Utah bentonite, the equilibrium constant proposed by themselves was independent of other ionic species, including hydrogen, present in the system.

For the purpose of theoretical analysis, it will be assumed that the equilibrium between two cations is independent of the presence of the third cation and that the simple mass-action law without the activity corrections applies to the equilibrium, in which case the exchanger should satisfy the following simultaneous equations,

$$K_{AB} = \frac{(\bar{m}_A)}{(\bar{m}_A)} \frac{(m_B)}{(\bar{m}_B)} \quad (2-24a)$$

$$K_{AC} = \frac{(\bar{m}_A)}{(\bar{m}_A)} \frac{(m_C)}{(\bar{m}_C)} \quad (2-24b)$$

$$\bar{m}_A + \bar{m}_B + \bar{m}_C = C.E.C., \quad (2-24c)$$

where all the cations are assumed to be the same valences.

Rearranging these equations, one can obtain the following expressions⁽²⁶⁾, which permit computation of the distribution coefficients, K_d , of each cation.

$$K_{d_A} = \frac{(C.E.C.) K_{o_{AB}} K_{o_{AC}}}{m_B K_{o_{AC}} + m_C K_{o_{AB}} + m_A K_{o_{AB}} K_{o_{AC}}}, \quad (2-25a)$$

$$K_{d_B} = \frac{(C.E.C.) K_{o_{AC}}}{m_B K_{o_{AC}} + m_C K_{o_{AB}} + m_A K_{o_{AB}} K_{o_{AC}}}, \quad (2-25b)$$

$$K_{d_C} = \frac{(C.E.C.) K_{o_{AB}}}{m_B K_{o_{AC}} + m_C K_{o_{AB}} + m_A K_{o_{AB}} K_{o_{AC}}}. \quad (2-25c)$$

If cation A is in trace concentration, Equation (2-25a) reduces to

$$K_{d_A} = \frac{(C.E.C.) K_{o_{AB}} K_{o_{AC}}}{m_B K_{o_{AC}} + m_C K_{o_{AB}}}. \quad (2-25d)$$

In the case of unsymmetrical exchange, in which the valences of the cations involved are not the same, the mathematical expressions for the system become more complicated. However, the manner of analyzing the system is similar.

2.6. Effects of Organic Compounds on Ion-Exchange Reactions of Clay Minerals

In general, deviation from an ideal ion-exchange equilibrium may be due to the interactions among the various components present in the system. These interactions can be either between one component and

others in the external solution phase, such as the formation of organic complexes of metal ions, or it can be the interaction between one component and the solid exchanger.

Effects of organic compounds on the ion-exchange reaction of soil minerals may be divided into two groups, one in which organic compounds interact with inorganic counter ions, especially metal ions, and the other in which the organic components may interact with soil mineral surfaces and thereby affect the ion-exchange properties of the soil minerals. The interaction of a certain organic cation with soil surfaces may be a simple ion-exchange reaction without affecting the soil exchange properties, or it may be that in the process of the exchange adsorption the soil's ion-exchange properties change.

2.6.1. Ion-Exchange Equilibria of Clay Minerals in the Presence of Sequestering Agents

In general, cation-exchange equilibria are strongly affected by the interaction⁽¹⁴⁾ of counter ions with other components in the solution phase. The interactions of cations with anions in the solution phase are particularly important, because anions are rather efficiently excluded from the solid exchanger phase, and thus the effects of these interactions in the solution phase are not compensated by that of similar interaction in the solid exchanger phase. The exchanger, in general, prefers those cations that associate less strongly with anions. This rule is illustrated by a typical example. Cation exchangers prefer other cations to Hg^{++} if the solution contains Cl^- , which form insoluble HgCl_2 .

Among other possible interactions of cationic radionuclides in

a soil environment, the formation of water soluble chelated compounds (sequestered compounds) is one of the most important reactions in regard to their transport through the soil medium, because the formation of water soluble chelated compounds of these radionuclides inhibits their adsorption on soil minerals. The formation of chelated compounds results in the inactivation of the counter ions by forming either neutral or even negatively charged metal chelates. The degree of the inactivation of a counter ion by a sequestering agent depends on the nature of the agent and the counter ion.

The general theoretical treatment of an ion-exchange equilibrium is valid whether or not chelated products are formed. The formation of chelated compounds can be treated as an additional, distinct reaction. The quantitative treatment of the ion-exchange equilibrium in the presence of sequestering agents is based on the known relations for the equilibria of the various chelated compounds. For a simple system in which the counter ions, A^{a+} and B^{b+} , are in equilibrium with an ion exchanger in the presence of sequestering agent, Y^{y-} , which forms chelated compound, AY^{a-y} , with only cation A^{a+} and does not interact with the exchanger, the distribution of the counter ion A^{a+} has to satisfy the following simultaneous equations,

$$K_{oAB} = \frac{(\bar{m}_A)^b}{(m_A)^b} \frac{(m_B)^a}{(\bar{m}_B)^a}, \quad (2-26a)$$

and

$$K_{AY} = \frac{(m_{AY})}{(m_A)(m_Y)}, \quad (2-26b)$$

where K_{AY} is the stability constant of the chelate compound, AY , and m_Y is the ionic concentration of organic ligand, Y^{Y-} , in the solution. Rearranging these equations in terms of the effective distribution coefficient, \overline{Kd}_A , that is, the ratio of the cation A^{a+} in the exchanger phase to its total concentration in the solution phase, the following expression is obtained,

$$\overline{Kd}_A = \frac{\overline{m}_A}{m_A + m_{AY}} = \frac{\left[K_{OAB} \left(\frac{\overline{m}_B}{m_B} \right)^a \right] \frac{1}{b}}{1 + m_Y K_{AY}}, \quad (2-27)$$

which shows the effect of the sequestering agent, (m_Y) , on the effective distribution coefficient, \overline{Kd}_A .

The case in which both cations, A^{a+} and B^{b+} , form chelated compounds with Y^{Y-} is more complicated. This situation occurs, for example, in the ion-exchange reaction of the counter ion pair $Sr^{++}-Ca^{++}$ in the presence of a sequestering agent. Equation (2-26) remains unchanged even if the competing counter ion B^{b+} forms a chelated compound. An exactly analogous relation holds for the effective distribution coefficient of B^{b+} , \overline{Kd}_B :

$$\overline{Kd}_B = \frac{\left[K_{OBA} \left(\frac{\overline{m}_A}{m_A} \right)^b \right] \frac{1}{a}}{1 + m_Y K_{BY}} \quad (2-28)$$

The ratio of two effective distribution coefficients gives the effective selectivity coefficient for the counter ion pair $Sr^{++}-Ca^{++}$ in the presence of sequestering agents.

$$\begin{aligned}\overline{K_o}_{AB} &= \frac{(\overline{Kd}_A)^b}{(\overline{Kd}_B)^a} \\ &= K_o_{AB} \times \frac{(1 + m_Y K_{BY})^a}{(1 + m_Y K_{AY})^b},\end{aligned}\quad (2-29)$$

where $\overline{K_o}_{AB}$ refers to the effective selectivity coefficient, and K_{BY} and K_{AY} are the stability constants of the chelate BY and AY.

It should be noted that in the derivation of these equations several assumptions are made: (1) sequestering agents do not interact with the solid exchanger, (2) sequestering agents form only one type of sequestered compound with each cation, and (3) the sequestered cations do not compete for the ion-exchange sites. In actual practice, the situation becomes much more complicated by the fact that certain agents do indeed interact with the solid exchanger, as will be shown in a later section, and in general sequestering agents form more than one type of sequestered compound with each cation. In addition, the stability of the sequestered compounds depends on the conditions of the system, such as its pH, which further complicates the theoretical analysis of the system.

2.6.2. Adsorption of Organic Compounds on Clay Minerals and Its Effects on Ion-Exchange Properties of These Clay Minerals

2.6.2.1. Organic Adsorption on Clay Surfaces

Interactions of organic compounds with clay minerals are surface reactions and are generally regarded as adsorption reactions. Interactions between clay surfaces and organic compounds may

be divided into two general types of adsorption, physical and chemical adsorption. Physical adsorption, or Van der Waals adsorption as it is often called, is due to dipole-dipole or ion-dipole interactions. Chemical adsorption is due to coulombic forces and results from bond formation between the adsorbent and adsorbate. A hydrogen bond ($-C-H \cdots$ clay surface) may be classified under either physical or chemical adsorption.

Organic molecules having a positive charge can be readily adsorbed on clay surfaces through an ion-exchange reaction. Hendricks⁽²⁷⁾ has indicated that when organic cations are adsorbed on clay surfaces, they are held on the surface by coulombic force, in addition to a Van der Waals force associated with the organic chain and the clay surface.

Since the clay-mineral surfaces are polar, when they are in contact with a solution containing polar organic compounds, the negative centers on the clay minerals attract the positive centers of the polar organic compounds. MacEwan⁽²⁸⁾ and Bradley⁽²⁹⁾ both reported that a large number of polar organic compounds can be adsorbed on the clay-mineral surfaces. From their X-ray diffraction data, it was concluded that these polar organic molecules lie flat between the sheets of expanding clay minerals (montmorillonite), and that there may be hydrogen bonding, $-C-H \cdots O$, between the chains of organic molecules and the oxygen atoms at the surface of the clay minerals.

2.6.2.2. Effects of Adsorbed Organic Compounds on Properties of Clay Minerals

When an organic molecule is adsorbed on a clay surface, it is expected that the surface properties of the clay mineral will be

changed. Such change in the surface characteristics may affect the ion-exchange properties of these clay minerals. The clay mineral properties that may be altered by organic adsorption are (a) the negative charge of the clay surface, (b) the active surface area of the clay mineral, (c) the blinding at the edge of the basal plane surface, (d) the bridging of the basal planes of the expanding clay minerals, and (e) the water sorption properties of the clay mineral surface. In terms of ion-exchange parameters, these effects may be (a) the reduction of the exchange capacity due to the permanent occupation of the exchange sites by strongly adsorbed organic cations or due to covering up of available exchange sites by a large, adsorbed organic molecule, and (b) the change in the selective properties of the clay mineral for hydrated metal ions resulting from the hydrophobic nature of the organic-adsorbed surfaces or the cross-linkage of the facing surfaces of the expanding clay mineral. In addition, a large organic molecule adsorbed at the edge of the basal plane surface of a clay mineral may form some type of physical barrier, which may interfere with inorganic ions entering the basal plane of the clay mineral.

(a) Effects of adsorbed organic molecules on the negative charge of clay surfaces

Certain organic cations are so strongly held on the clay surfaces that once adsorbed, inorganic cations of the same molar concentration may not replace these adsorbed organic cations. This results in the net reduction of total negative charge on the clay surface, and hence may result in the reduction of exchangeable sites. In general, the larger organic cations are more strongly adsorbed because in addition to

the coulombic forces, the Van der Waals forces are greater.

(b) Effects of adsorbed organic compounds on active surface area of clay minerals

Hendricks⁽²⁷⁾ has shown when large organic cations are adsorbed on a clay surface, even though they are more strongly adsorbed than smaller ones, they occupy fewer exchange sites, indicating cover-up effects. A large organic cation, when it is adsorbed on a clay surface, may physically cover up more than one exchange site. On the average, the effective area of each exchange site on montmorillonite is about 80 to 100 Å². If an organic cation which has an effective area larger than 100 Å² is adsorbed on a montmorillonite surface, this organic cation may cover up more than one exchange site, thereby reducing the active surface area of the clay mineral.

(c) Effects of adsorbed organic compounds on expanding characteristics of clay minerals

Hendricks⁽²⁷⁾, Bradley and Grim⁽³⁰⁾, Jordan⁽³¹⁾, and many other investigators have found that when organic compounds are adsorbed on the interlayer surfaces of expanding clay minerals, a definite pattern of interlayer spacing exists, which depends on the size and concentration of the organic compound. When an organic molecule with more than one cationic group is adsorbed on the interlayer surface of the expanding clay minerals such as montmorillonite, this organic molecule may act to tie two facing surfaces together by adsorbing on both surfaces.

In montmorillonite, in the early stages of swelling, the interlayer spacing increases stepwise (Crystalline swelling). Stable interlayer

distances of about 9.5, 12.4, 15.4, 19.0, and 22.5 Å have been found by X-ray diffraction analysis⁽³²⁾. These spacings are common to almost all ionic forms. However, with strongly hydrated counter ions such as Li^+ , the stages of crystalline swelling are finally overcome as more solvent (water) molecules are adsorbed. Beyond 40 Å, the interlayer spacing increases continuously, and the material behaved like a gel. Montmorillonite⁽²⁹⁾ whose interlayer surfaces were covered with methylamine and glycerol showed the interlayer spacing of 12.7 and 17.7 Å, respectively. This indicated that when an organic cation about 10 Å in size having more than one cationic group is adsorbed on two facing surfaces of interlayer, the adsorbed organic may possibly limit the expanding of the interlayer planes. The change in the interlayer spacing of expanding clay minerals may affect the mobility of other cations on the interlayer surface, and thus affect the selectivity of this clay mineral for certain inorganic cations.

(d) Effects of adsorbed organic compounds on water-sorption properties of clay minerals

In general, when organic molecules are adsorbed on a clay mineral surface, adsorbed water on the surface will be displaced. The displacement of water molecules from the surface and the covering up of the oxygen layer with the chain of the organic molecules will have tendency to alter the clay surface from its hydrophilic to hydrophobic character. The water-adsorbing properties of montmorillonite are gradually reduced as the basal surfaces of the mineral are coated with organic molecules. Geiseking⁽³³⁾ reported that when montmorillonite clay minerals were saturated with a variety of organic cations, they lost

their tendency to swell by water sorption. The degree of alteration in water=sorption properties of clay minerals due to organic adsorption will depend on the degree of saturation and the nature of the organic molecules on the clay mineral surface. The change of the clay surface from hydrophilic to hydrophobic may affect the selective properties of the clay exchange medium for hydrated inorganic cations.

3. MATERIALS AND EXPERIMENTAL PROCEDURE

3.1. Materials Used

Since the purpose of this investigation was to study various interactions of natural and pure organic compounds with soil constituents and the effects of these interactions on ion-exchange reactions between cationic radionuclides and soil exchange media, chemicals and soil materials were so selected that they would be closely related to the actual soil environmental conditions and yet still be able to demonstrate various interactions involved in the system.

Due to difficulties of selecting uniform and homogeneous soil materials which would give reproducible experimental results, relatively pure clay minerals were selected instead of soil materials for this investigation. Because the major fraction of the ion-exchange properties of natural soil materials is probably embodied in the clay fraction, it is common practice to use clay minerals in the study of the ion-exchange properties of soils.

Because of the unknown complexity of naturally-occurring organic compounds, it is virtually impossible to study individual interactions of natural organic compounds. The probable interactions were studied using several groups of carefully selected pure organic compounds which are known to be present or similar to that present in the natural environment.

3.1.1. Properties of Clay Minerals

For the materials representing soils, montmorillonite and

illite were chosen because they represent the large fraction of clay minerals in natural soil. It was hoped that using two clay minerals with different mineralogical characteristics, the individual physical forces and parameters that govern the ion-exchange properties of soils would be investigated. Montmorillonite (Mississippi) and illite (Fithian, Illinois) used in this investigation were obtained from the Illinois State Geological Survey. The X-ray diffraction analysis of these clay minerals showed considerable amounts of impurity. The approximate estimate of the purity from the X-ray data are summarized on Table 1.

TABLE 1
APPROXIMATE PURITY OF CLAY MINERALS USED

Contents	Mississippi Montmorillonite	Fithian Illite
Montmorillonite	80-90%	10%
Illite	0	55%
Chlorite	0	12%
Kaolinite	5-10%	0%
Quartz and other impurity	5-10%	23%

3.1.1.1. Montmorillonite

Montmorillonite constitutes one of the most widely occurring clay minerals. The structure of the montmorillonite unit consists of two silica tetrahedral sheets and a central alumina octahedral sheet. Montmorillonite's theoretical formula⁽¹³⁾ is $(\text{OH})_4\text{Si}_8\text{Al}_4\text{O}_{20}\cdot n\text{H}_2\text{O}$; however, some fraction of the Si^{4+} ions in the lattice are replaced by Al^{3+} and Mg^{2+} . Furthermore, the lattice is always unbalanced as a result of these substitutions, and has a net positive charge deficiency, depending

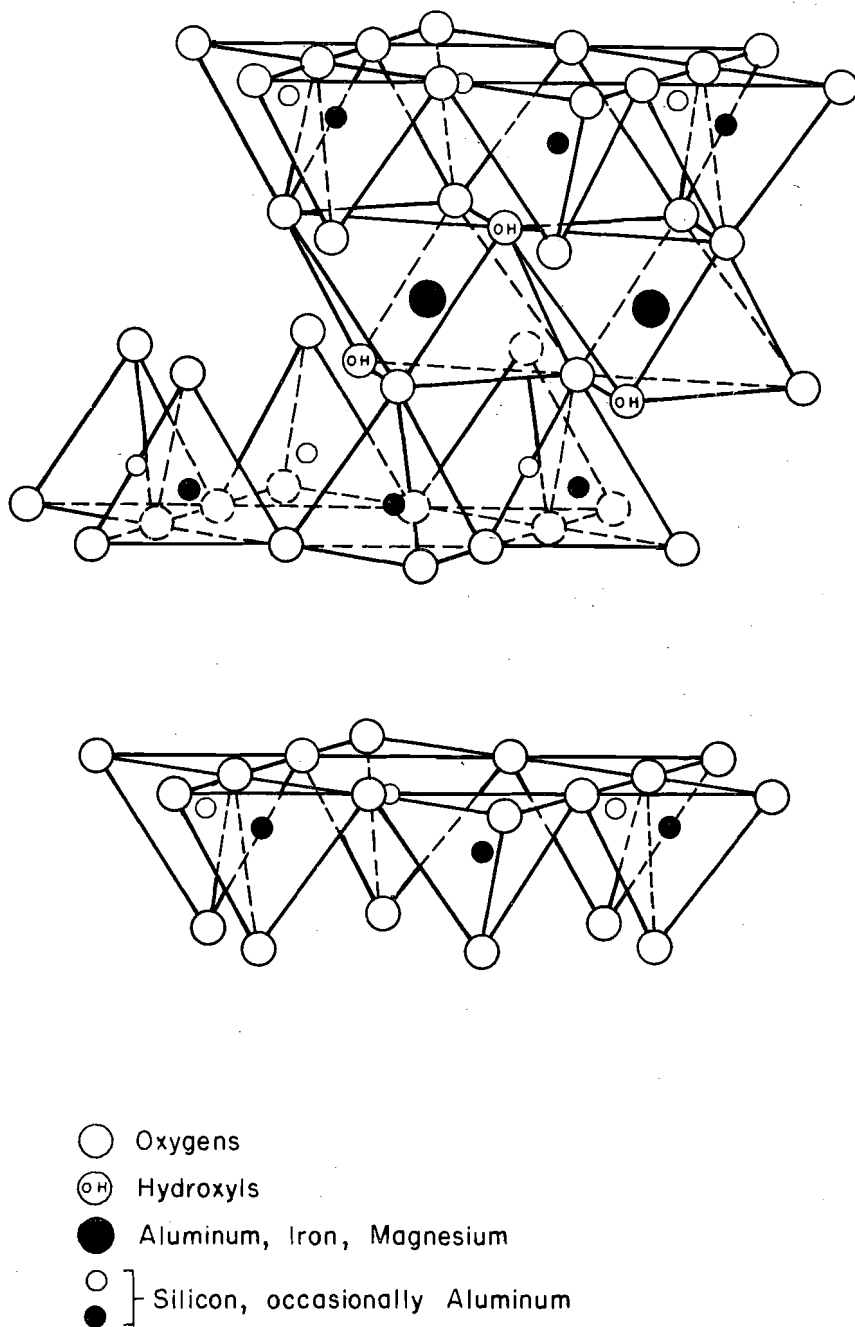


FIG. 1 DIAGRAMATIC SKETCH OF THE STRUCTURE OF MONTMORILLONITE.

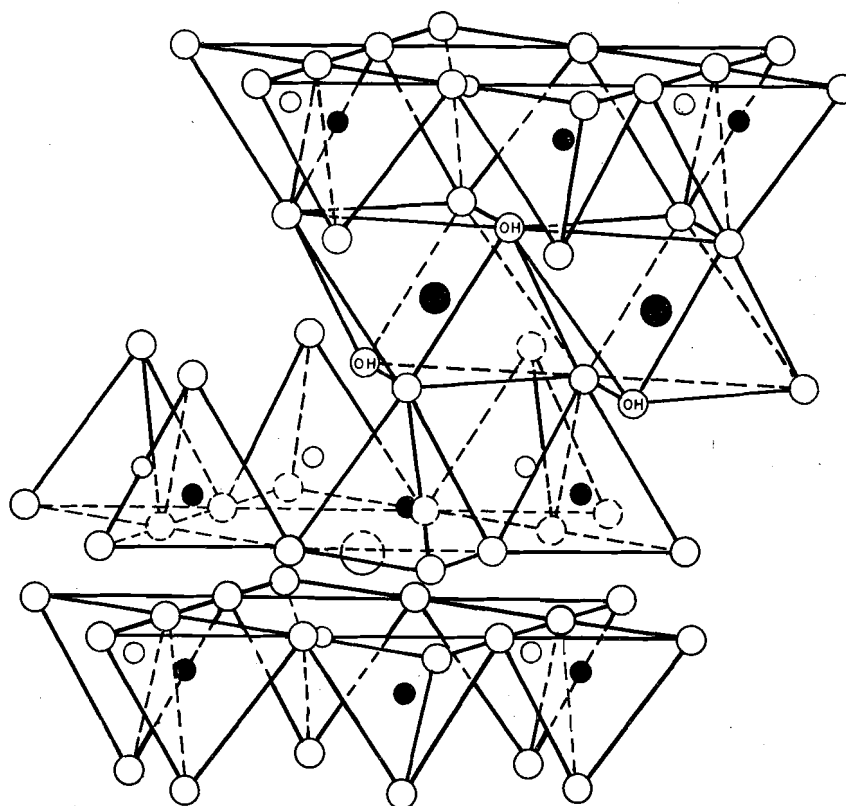
minerals, most of the exchangeable sites are at the edges which are caused by broken bonds around the edges. Figure 2 shows a diagrammatic sketch of illite.

3.1.1.3. Treatment of Clay Minerals

Powdered clay minerals obtained from the Illinois Geological Survey contained exchangeable cations in many different forms, as they would be in natural conditions. In order to make these clay minerals monoionic form (Ca^{++} , Mg^{++} , Na^+ , and Sr^{++}), the clay minerals (montmorillonite and illite) were first repeatedly saturated with 1.0 N solutions of CaCl_2 , MgCl_2 , NaCl , and SrCl_2 in separate containers, followed by washing with demineralized water until the conductivity measurements of the centrifuged supernatants indicate no free electrolytes present in the clay suspensions.

The particle sizes less than 2μ were fractionated from these monoionic clay suspensions by a centrifuge separation method⁽³⁴⁾. In order to make sure these clay mineral suspensions were in monoionic forms, these clay mineral suspensions were passed through ion-exchange columns packed with Amberlite-120 in the corresponding ionic forms.

The aging effects on the stability of these monoionic clay mineral suspensions were determined by the periodic measurements of their pH and conductivity. Whenever the suspension showed high conductivity, indicating eluted free electrolytes in the suspension, the clay suspension was retreated to the monoionic form.



- Oxygens
- ⊙ Hydroxyls
- Aluminum
- ⊙ Potassium
- ⊙ } Silicons (One fourth replaced by aluminum)

FIG. 2 DIAGRAMATIC SKETCH OF THE STRUCTURE OF MUSCOVITE TYPE ILLITE.

3.1.2. Organic Compounds Used

3.1.2.1. Pure Organic Compounds

In the selection of pure organic compounds for this investigation, an effort was made to select those organic compounds which were known to be present in the natural environment and also to represent a variety of organic compounds with different chemical and physical properties, so that the various interactions with both clay minerals and metal ions would be adequately represented. The groups of pure organic compounds used in this investigation are sequestering agents, organic cations, and polar organic compounds.

Sequestering agents such as citrate, tartrate, and EDTA were used to study the interaction of these organic compounds with metal ions and the effects of the interactions on the ion-exchange equilibrium between the metal ions and clay minerals.

Cationic and polar compounds (methylamine, dodecylamine, methylene blue, arginine, and sucrose) were used to investigate the adsorption of these organic compounds on clay mineral surfaces and their effects on the ion-exchange properties of the clay minerals. The chemical and physical properties of these pure organic compounds are summarized on Tables 2 and 3.

3.1.2.2. Mixture of Organic Compounds in Natural Environments

The naturally occurring organic compounds used in this investigation include organics extracted from ground water and surface soil materials. The organic compounds extracted from ground water

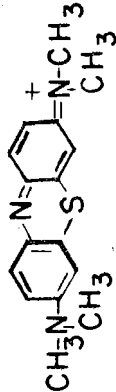

TABLE 2

CHEMICAL AND PHYSICAL PROPERTIES OF ORGANIC ANIONS (35)

Compound and formula	Ionization Constants		Stability Constants of Metal Chelates			
	$K_n = \frac{(H^+) (H_{n-1}Y^-)}{(H_nY)}$		Ca^{++}	Mg^{++}	Sr^{++}	Zn^{++}
tartaric acid, 150.09	$K_2=10^{-2.88}$	$\frac{(CaHY^+)}{(Ca^{++})(HY^-)}$	$10^{1.1}$	$10^{0.92}$	$10^{0.91}$	$10^{1.44}$
$\begin{array}{c} HO \quad OH \\ \quad \\ HO_2C-CH-CH-CO_2H \end{array}, H_2Y$	$K_1=10^{-3.94}$	$\frac{(CaY)}{(Ca^{++})(Y^{2-})}$	$10^{1.8}$	$10^{1.4}$	$10^{1.65}$	$10^{12.68}$
citric acid, 192.12	$K_3=10^{-3.08}$	$\frac{(CaHY)}{(Ca^{++})(HY^{2-})}$	$10^{3.0}$	--	--	--
$\begin{array}{c} CO_2H \\ \\ HO_2C-CH_2-\dot{C}-CH_2-CO_2H, H_3Y \\ \\ HO \end{array}$	$K_2=10^{-4.66}$	$\frac{(CaY^-)}{(Ca^{++})(Y^{3-})}$	$10^{3.22}$	--	$10^{2.7}$	$10^{4.08}$
	$K_1=10^{-5.49}$					
EDTA, 292.254	$K_4=10^{-2.0}$	$\frac{(CaHY^-)}{(Ca^{++})(HY^{3-})}$	$10^{3.51}$	$10^{2.28}$	$10^{2.7}$	--
$\begin{array}{c} HOOC-CH_2 \quad H_2C-COOH \\ \quad \quad \\ N-CH_2-CH_2-N \\ \quad \quad \\ HOOC-CH_2 \quad H_2C-COOH \end{array}, H_4Y$	$K_3=10^{-2.67}$	$\frac{(CaY^{2-})}{(Ca^{++})(Y^{4-})}$	$10^{10.59}$	$10^{8.69}$	$10^{8.63}$	$10^{16.5}$
	$K_2=10^{-6.16}$					
	$K_1=10^{-10.26}$					
arginine, 174.21	$K_1=10^{-12.48}$	None				42

TABLE 3

CHEMICAL AND PHYSICAL PROPERTIES OF ORGANIC CATIONS (35)

Compounds and Formula	Molecular Weight	Ionization Constants $K_n = \frac{(H^+) (YH_{n-1}^{n-1+})}{(YH_n^{n+})}$
methylaniline <chem>CH3-NH2</chem>	31.06	$10^{-10.72}$
dodecylamine <chem>C12H25NH2</chem>	185.36	$10^{-10.63}$
methyleure blue 	319.87	∞
arginine 	174.21	$K_1 = 10^{-9.08}$ $K_2 = 10^{-2.17}$

were a portion of those used in the experiments conducted by L. Robinson⁽³⁶⁾ at the University of Illinois in 1962.

The water soluble organic compounds in surface soil materials were extracted from soil materials obtained from a woody area. Approximately 2,000 grams of soil material which contained 5% vegetable decaying matter were placed in a 4-liter bottle containing 3 liters of demineralized water. After being shaken in the bottle for two days, the samples were centrifuged, followed by filtration through a 0.45 μ membrane filter. The dark brown filtered solution was evaporated at 50°C under vacuum until only 100 ml of the solution were left. The soil organic extracts probably contained metal ions either as free electrolytes or as metal ions chemically bound to the natural organic compounds. To remove the free metal ions the organic extracts were dialyzed against running demineralized water. The metal ions of higher valence that might have been chemically bound to the natural organic compounds were exchanged into Na^+ form by passing the extracts through an ion-exchange column previously saturated with Na^+ ions. Before the extracts were passed through the ion-exchange column, NaOH was added to the extracts to raise the pH value to 8.0, so that the organic cations would not be adsorbed on the column.

The chemical properties of these two extracts may have been somewhat different, for the ground water had passed through soil media for some distance, which may have caused this extract to be high in those organic constituents that do not readily interact with soil minerals. On the other hand, the organics extracted from the woody surface soils may have contained the organic compounds that do readily interact with soil minerals.

It should be noted, however, that as a result of the inefficient extraction method used in this investigation these organic extracts represented only a fraction of the probable constituents of the natural organic compounds.

3.2. Experimental Procedure

3.2.1. Analytical Methods and Equipment

In all experiments reactions were carried out in 6-ounce (180 ml), Armstrong prescription bottles. The bottles containing 50 ml of solution were agitated for 7 to 18 hours, which was found experimentally to be sufficient for equilibrium to be reached, by tumbling end-over-end on a mixing wheel at a speed of 5-10 rpm. After equilibrium was reached, 30 ml of the solution were transferred into a plastic centrifuge tube for phase separation and chemical analysis. The remaining volume was used for the measurement of the final pH of the solution.

Because the concentrations of samples involved in the experiments were too low for conventional chemical analyses, whenever possible radiotracer techniques were employed, in which one or more of constituents were labelled with radiotracers of the very same chemical compounds. By the combination of the radioassay analysis of the solution phase and an overall material balance, the distributions of various constituents of the system were analyzed.

For all the experiments involving strontium ion, the solutions were labelled with the gamma-emitting radioisotope, Sr^{85} . The strontium ion concentrations in the solution phase were determined by counting 10-ml

samples in plastic counting tubes with a gamma scintillation counter.

Whenever possible pure organic chemicals used for reaction studies were also labelled with C^{14} radiotracer of the very same compounds. The organic concentration in the solution phase was determined by counting the C^{14} activity of the solution with a liquid scintillation counter. The samples to be counted by the liquid scintillation counter were prepared by dissolving 3 ml of aqueous samples into 15 ml of the scintillation liquid.

The scintillation liquid was prepared by dissolving 7 grams of PPO (2,5,-Diphenyloxazole), 0.28 grams of POPOP (p-bis(2-(5-phenylox-azoly1))-benzene), and 75 grams of naphthalene in the mixture of 875 ml dioxane and 125 ml Cellosolve (ethylene glycol monoethyl ether). This composition of the scintillation liquid was experimentally determined to give the best efficiency (46%) for 3 ml of aqueous sample in 15 ml of the liquid.

3.2.2. Ion-Exchange Reactions

3.2.2.1. Exchange Capacity

Ion-exchange capacity is one of the most important parameters governing the ion-exchange equilibria of clay minerals. The knowledge of the exchange capacity is indispensable for the evaluation of the ion-exchange equilibrium between clay minerals and various counter ions. In general, reported ion-exchange capacities are known to vary according to the laboratory procedure employed to determine them, and therefore a method should be chosen duplicating as nearly as possible the actual conditions of the system to which the results are to have application.

A method of actual exchange of counter ions with the radioisotope of concern was employed in this investigation. However, for comparative purposes, other methods such as the ammonium acetate method^(37, 38) and the methylene blue method⁽³⁹⁾ were also used. The method for the determination of ion-exchange capacity used in this investigation is primarily based on the exchange of Sr^{++} ion on Sr-clay minerals by the radioisotope, Sr^{85} . When Sr-clay minerals are added to a solution containing Sr^{++} (m_{Sr}^0) and Sr^{85} (cpm^0), isotopic replacement will occur until the isotopic ratio ($\text{Sr}^{85}/\text{Sr}^{++}$) is the same in both the exchanger and the solution phases. Knowing the total Sr^{85} (cpm^0) added into the system, the amounts of Sr^{++} in the exchanger phase are determined from the following relationship,

$$\frac{(\text{cpm}_s)}{(\text{cpm}^0)} = \frac{m_{\text{Sr}}}{m_{\text{Sr}} + \bar{m}_{\text{Sr}}} \quad (3-1)$$

Equation (3-1) may also be written in the form,

$$\frac{(\text{cpm}^0)}{(\text{cpm}_s)} - 1.0 = \bar{m}_{\text{Sr}} \times \frac{1.0}{m_{\text{Sr}}} \quad (3-2)$$

where (cpm^0) and (cpm_s) refer to the Sr^{85} activities of the total and solution phase, respectively.

If the ratio of the radioactivity in the exchange phase to that in the solution phase ($\text{cpm}^0/\text{cpm}_s - 1.0$) is to be plotted as a function of the value of $1.0/m_{\text{Sr}}$, the form of Equation (3-2) is a straight line whose slope is \bar{m}_{Sr} . From the known value of m_{Sr} and radioassay data, the

exchange capacities are determined.

In the determination of exchange capacities, 0.05 to 0.2 grams of monoionic Sr-clay minerals (montmorillonite and illite) were equilibrated with 50 ml of $\text{Sr}(\text{NO}_3)_2$ solution labelled with Sr^{85} . The exchange capacities were determined as a function of Sr^{++} concentration varying from 1×10^{-4} to 1×10^{-2} N. At the higher concentration, Sr^{++} in the exchanger phase becomes insignificant compared to the solution concentration, and hence the accuracy of the determination is reduced.

3.2.2.2. Equilibrium Constants

For the prediction of the distribution and transport of radionuclides disposed to an environment, knowledge of equilibrium reactions between these radionuclides and soil materials is essential. In this investigation, an effort was made to apply the various ion-exchange theories for evaluating the most reliable equilibrium constants.

The ion-exchange reactions performed for the evaluation of the equilibrium constants included the reaction in which (1) Sr^{++} ions are replacing Ca^{++} ions, (2) Sr^{++} ions are replacing Mg^{++} ions, and (3) Sr^{++} ions are replacing Na^+ ions on both montmorillonite and illite minerals.

In order to examine the reversibility of the exchange reactions, all the equilibria were approached from both directions. For the determination of the equilibrium constant for the reaction where Sr^{++} ions were competing with Ca^{++} ion for exchange sites on the clay mineral, both Ca-clays and Sr-clays were used. Similarly, Mg-clays and Sr-clays, and Na-clays and Sr-clays were used for the determination of the equilibrium constants for the reactions where Sr^{++} ions were competing with Mg^{++} ions

and where Sr^{++} ions were competing with Na^+ ions for the exchange sites on clay minerals.

The equilibrium constants were determined as a function of the counter ion concentrations at room temperature. For the determination of the equilibrium constants for the reaction where Sr^{++} ions were replacing Ca^{++} on Ca-clay minerals, the initial concentrations of strontium and calcium ions (m_{Sr}^0 and m_{Ca}^0) were varied from 10^{-6} to 10^{-3} N. The maximum concentration was limited by the fact that at higher concentration, the radioassay analysis became difficult. The concentration distribution of the counter ions in the liquid phase was determined by counting 10 ml of the centrifuged aqueous sample with a gamma-scintillation counter.

When a Ca-clay was used for the determination of the equilibrium constant for the reaction in which the counter ions Ca^{++} and Sr^{++} were in equilibrium with the clay minerals, the concentration distributions of the counter ions were determined from the following relationships,

$$m_{\text{Sr}}^0 = \bar{m}_{\text{Sr}} + m_{\text{Sr}} \quad (3-3a)$$

$$m_{\text{Ca}}^0 + \text{C.E.C.} = \bar{m}_{\text{Ca}} + m_{\text{Ca}} \quad (3-3b)$$

$$\text{C.E.C.} = \bar{m}_{\text{Sr}} + \bar{m}_{\text{Ca}} \quad (3-3c)$$

$$\frac{\text{cpm}_s}{\text{cpm}^0} = \frac{m_{\text{Sr}}}{m_{\text{Sr}}^0}, \quad (3-3d)$$

where m_{Sr}^0 , m_{Ca}^0 , and C.E.C. are the concentrations of strontium, calcium, and Ca-clay initially added to the system, and m_{Ca} , m_{Sr} , \bar{m}_{Ca} , and \bar{m}_{Sr} are

the final concentration distributions. cpm_s refers to the Sr^{85} activity of the final solution phase, while cpm^o is the total Sr^{85} activity of the system.

By rewriting Equation (3-3) in terms of the radioassay data, the following relationships were obtained,

$$m_{\text{Sr}} = m_{\text{Sr}}^o \frac{\text{cpm}_s}{\text{cpm}^o} \quad (3-4a)$$

$$\bar{m}_{\text{Sr}} = m_{\text{Sr}}^o \left(1 - \frac{\text{cpm}_s}{\text{cpm}^o} \right) \quad (3-4b)$$

$$\bar{m}_{\text{Ca}} = \text{C.E.C.} - m_{\text{Sr}}^o \left(1 - \frac{\text{cpm}_s}{\text{cpm}^o} \right) \quad (3-4c)$$

$$m_{\text{Ca}} = m_{\text{Ca}}^o + m_{\text{Sr}}^o \left(1 - \frac{\text{cpm}_s}{\text{cpm}^o} \right), \quad (3-4d)$$

which give the complete concentration distribution of the counter ions, Sr^{++} and Ca^{++} , in both the exchanger and solution phases. The equilibrium constant for the system containing other pairs of counter ions were determined in a similar manner.

3.2.2.3. Equilibrium Reactions of Heterogeneous Clay Mixtures

As mentioned in Section 2.4., when the soil exchange medium is a mixture of clay minerals or a mixture of different types of exchange sites, the equilibrium constants depend on the experimental conditions.

Experiments were performed with a mixture of montmorillonite

and illite to examine the effects of nonhomogeneity of the exchange media. For the ion-exchange reaction in which Sr^{++} ions were replacing Mg^{++} ions on the mixture of Mg-montmorillonite and Mg-illite, the equilibrium constants were determined as a function of the counter ion concentration. The effective equilibrium constants, \bar{K}_{SrMg} , were experimentally determined using Equation (2-22). These values were compared with the effective equilibrium constant computed from Equation (2-23). The equilibrium constants for the exchange between Sr^{++} and Na^+ were also investigated with various compositions of the mixture. The experimental procedure was similar to that described in Section 3.2.2.2.

3.2.2.4. Ion-Exchange Equilibrium in a Multicomponent System

When a trace quantity of radioactive strontium ion comes in contact with soil materials, strontium ions will compete for the exchange sites on the soils with a number of other gross cations present in the system. Various ion-exchange theories have been found satisfactory for describing ion-exchange reactions involving a pair of counter ions. However, a theory will have little practical value if its application is limited to a system having only one pair of cations. Use of the mass-action expression (without activity corrections) for describing the equilibrium conditions of a multicomponent system was previously discussed in Section 2.5. The application of the mass-action expressions for a multicomponent system was next subjected to experimental test.

Experiments were performed to examine the ion-exchange reactions in a multicomponent system containing Ca^{++} , Mg^{++} , Na^+ , and Sr^{++} . Applying the simultaneous equations (2-24) described in Section 2.5, the strontium

concentration in the solution phase can be shown to be,

$$m_{Sr} = m_{Ca}^o + m_{Mg}^o + m_{Na}^o + m_{Sr}^o - \frac{m_{Na}^o}{1 + \left(\frac{1}{K_{O_{SrNa}}} \left(\frac{m_{Sr}^o - m_{Sr}}{m_{Sr}} \right)^{1/2} \right)} - \frac{m_{Ca}^o + C.E.C.}{1 + \frac{1}{K_{O_{SrCa}}} \left(\frac{m_{Sr}^o - m_{Sr}}{m_{Sr}} \right)} - \frac{m_{Mg}^o}{1 + \frac{1}{K_{O_{SrMg}}} \left(\frac{m_{Sr}^o - m_{Sr}}{m_{Sr}} \right)} \quad (3-5)$$

where m_{Ca}^o , m_{Mg}^o , m_{Na}^o , and m_{Sr}^o are the total concentrations of these cations added to the system, and C.E.C. is the amount of Ca-clay added to the system.

The experimental data for Sr^{++} distribution in the system were compared with the value computed from Equation (3-5).

3.2.2.5. pH Effects on Ion-Exchange Equilibria

In general, the expressions for the mass-action law have been found satisfactory for the exchange between a large number of ion pairs over wide variation in ion concentration and in various amounts of exchange media; however, a notable exception was encountered in ion pairs involving hydrogen, H^+ . Krishnamoorthy and Overstreet⁽²⁴⁾ found that the equilibrium conditions involving hydrogen ions can not be predicted by any theory proposed thus far. A possible reason for the behavior of hydrogen may be found in the fundamental assumptions necessary for formulation of any ion-exchange equation. Most important of these is

the assumption that either the specific interaction energies of the ion in question with the charged surface (clay surface) are constant over a wide variety of conditions, or their differences for a chosen pair of ions is constant. Unless this condition is fulfilled no ion-exchange formulation based on concentration terms is possible. For pairs of ions which interact with the surface by purely electrostatic forces, this assumption appears reasonable (as will be discussed in a later section). On the other hand, for ions that may be held to the surface by other chemical bonds as well as by electrostatic forces, it seems that the interaction will depend on their amounts in the solid exchanger phase.

For the purpose of examining the effects of hydrogen ion on the ion-exchange parameters of clay minerals used in this investigation, the ion-exchange reactions of the counter ion pairs $\text{Sr}^{++}\text{-Ca}^{++}$ and $\text{Sr}^{++}\text{-Mg}^{++}$ in the presence of hydrogen ions were investigated. Possible interactions of hydrogen ion other than an ion exchange reaction were examined by testing the equivalence of adsorbed hydrogen and eluted strontium ion in the reaction where the pair of ions, Sr^{++} and H^+ , were in equilibrium with Sr-clay minerals. The strontium ions removed from the Sr-clay minerals by hydrogen ions were computed from the following relationships,

$$\text{Eluted } \text{Sr}^{++} = m_{\text{Sr}} - m_{\text{Sr}}^{\circ} \quad (3-6a)$$

$$\frac{\text{cpm}_s}{\text{cpm}^{\circ}} = \frac{m_{\text{Sr}}}{m_{\text{Sr}}^{\circ} + \text{C.E.C.}} \quad (3-6b)$$

$$\text{Disappeared } \text{H}^+ \text{ ions, } \Delta \text{H}^+ = m_{\text{H}}^{\circ} - m_{\text{H}} \quad (3-6c)$$

$$\text{pH} = -\log m_{\text{H}} \quad (3-6d)$$

$$\text{Disappeared OH}^- \text{ ions, } \Delta\text{OH}^- = \frac{10^{-14}}{m_{\text{H}}} \quad (3-6e)$$

Here m_{Sr} and m_{H} represent the final concentrations of strontium and hydrogen ions in the solution phase, and m_{Sr}^0 , m_{H}^0 , and m_{OH}^0 represent the initial amounts of strontium, hydrogen, and hydroxyl ions added to the system.

3.2.2.6. Effects of Sequestering Agents on Ion-Exchange

Reactions of Clay Minerals

Many organic anions which commonly occur in natural water⁽⁴⁰⁾, as well as in soils, form stable chelates with metal ions. Among these reagents may be listed citrate, tartrate, malate, high-molecular-weight organic anions with polycarboxyl groups, and various amino acid anions. The exact nature of these natural sequestering agents is not always known. These organic ligands (sequestering agents) are believed to be either the synthesis products of microorganisms or bacterial decay products of vegetable matter in soils.

As a result of the unknown complexity of their composition, it is impossible to examine individual interactions involved with sequestering agents in organic mixture obtained from natural environment. The specific interactions of the various sequestering agents with metal ions and their effects on the ion-exchange reactions between metal ions and soil materials were studied using chemically pure sequestering agents. These sequestering agents include citrate, tartrate and EDTA

(ethylenediaminetetraacetic acid).

The effects of these sequestering agents on the equilibrium distribution of the various counter ion pairs ($\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$, $\text{Sr}^{++}\text{-Zn}^{++}$, and $\text{Sr}^{++}\text{-Na}^{+}$) in equilibrium with clay minerals were investigated at concentrations of these reagents varying from a trace quantity to that approximately equivalent to twice the total metal ions in the system.

The sequestering agents were labelled with carbon¹⁴ tracers to determine their concentration distribution by a radioassay analysis. The adsorption of the ligands on clay surface was computed from the radioassay data.

3.2.2.7. Effects of Adsorbed Organic Compounds on Ion-Exchange Reactions of Clay Minerals

The probable effects of adsorbed organic compounds on the ion-exchange properties of clay minerals were discussed in Section 2.6.2. A variety of organic compounds with different physical and chemical properties were used for the investigation of their effects on the ion-exchange properties of clay minerals. These organic compounds may be further divided into four groups, each having its typical properties: (a) monocationic amine compounds (methylamine and dodecylamine), (b) a strong cationic compound (methylene blue), (c) a polycationic compound (arginine), and (d) a polar organic compound (sucrose).

The probable effects of these organic compounds on the ion-exchange properties of clay minerals were studied by the comparison of the equilibrium distribution of counter ion pairs ($\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$,

and $\text{Sr}^{++}=\text{Na}^+$ in two systems, one in which the counter ions were in equilibrium with clay minerals only and the other in which the counter ions were in equilibrium with clay minerals in the presence of these organic compounds.

(a) Methylamine and Dodecylamine

Monocationic amine compounds, methylamine and dodecylamine, were used to study the effects of these organic compounds as a function of the organic chain sizes and concentrations. From the reactions in which Sr^{++} ions on Sr-clay minerals were being replaced by these organic cations, the relative selectivities of the clay minerals for these organic cations with respect to Sr^{++} ions were investigated. The effects of these organic compounds on the ion-exchange reactions of various counter ion pairs were examined as a function of the organic concentration varying from 10^{-5} to 10^{-3} N, which in terms of milligrams per liter is 0.31 to 31 mg/l for methylamine. The concentration distribution of Sr^{++} ions and organic compounds were determined by the tracer technique using Sr^{85} and C^{14} labelled compounds.

(b) Methylene Blue

Because of their strong cationic characteristics, methylene blue ions are irreversibly adsorbed on clay minerals and cannot be eluted from the clay surface by any inorganic cation in reasonable concentration. Methylene blue ions were used to blanket various portions of the exchange sites on clay minerals and to study the effects of this covering up on the ion-exchange reactions of these clay minerals with various cation pairs. The monoionic clay minerals whose surfaces were covered with

methylene blue ions (20%, 40%, 60%, and up to 80%) were subjected to reactions with various counter ion pairs, and the equilibrium constants were calculated based on the uncovered exchange sites. The effects of the presence of the large organic molecules, that is, methylene blue ions adsorbed on the basal plane surfaces of the clay minerals, on the ion-exchange properties of these clay minerals were investigated. The change in the selectivity of the clay minerals for various counter ions due to the adsorption of methylene blue ions was investigated as a function of the portion of the covered up surfaces.

(c) Arginine

The arginine molecule has two cationic groups which may be adsorbed on the two facing surfaces of the basal planes, and thereby, limit the c-spacing of expanding clay minerals (montmorillonite) by a bridging effect. The fixation of the c-spacing of expanding clay minerals may affect the mobility of the inorganic counter ions between the facing layer surfaces. The ion-exchange reactions of clay minerals with various counter ions in the presence of arginine molecules were studied to investigate the effects of c-spacing fixation of expanding clay minerals. The equilibrium distribution of the counter ion pairs, $\text{Sr}^{++}\text{-Mg}^{++}$ and $\text{Sr}^{++}\text{-Na}^+$, in equilibrium with clay minerals whose surfaces were partially covered with arginine molecules were examined as a function of the arginine concentration.

(d) Polar compound, Sucrose

The adsorption of polar organic compounds on clay surface may

not affect the charge distribution of the surface; however, it may affect other properties governing the ion exchange reaction of these clay minerals. The effects of polar compounds on the ion-exchange equilibrium between clay minerals and the counter ion pairs, $\text{Sr}^{++}\text{-Mg}^{++}$ and $\text{Sr}^{++}\text{-Ca}^{++}$, were investigated with sucrose as the polar compound. The adsorption of sucrose molecules on clay surfaces was determined by radioassay analysis of the C^{14} activity of the solution phase. The amounts of adsorbed sucrose molecules were calculated from the difference of C^{14} activities in the total system and the solution phase. The experiments were performed to examine the effects of sucrose on changes in inorganic counter ion distribution in the presence of sucrose.

3.2.2.8. Effects of Natural Organic Compounds on Ion-Exchange Reactions of Clay Minerals

The natural organic compounds used in this investigation included water-soluble organic compounds extracted from both ground water and woody surface soils.

The experiments with these organic extracts were performed in a similar manner as those with pure organic compounds; however, due to the unknown compositions and difficulties with the chemical analyses of these extracts, the distribution of the extracts in the system was not analyzed. The effects of the extracts on ion-exchange reactions of clay minerals were investigated on the basis of the total organic added into the system. The ion-exchange reactions of the counter ion pairs, $\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$, and $\text{Sr}^{++}\text{-Na}^{+}$, in equilibrium with clay minerals were studied in the presence of these extracts. The effects of the extracts were examined in terms of the change in the counter ion distributions.

4. ION-EXCHANGE EQUILIBRIUM IN ABSENCE OF ORGANICS;

RESULTS AND DISCUSSION

4.1. Treatment of Clay Minerals

Clay suspensions (Mississippi montmorillonite and Fithian Illite) converted into various monoionic forms were stored in polyethylene bottles. To determine the aging effects on their stabilities, pH and conductivity of the supernatant of the centrifuged clay suspension were periodically measured. The values of the measurements are summarized in Table 4.

The measurements of the conductivity indicated that after one month of aging, the illite suspension contained considerable amounts of free electrolyte. The instability of the illite suspension suggested that the impurity contained in Fithian illite might have been dissolved. The measurements of pH indicated that hydrogen ions were not involved in the instability of the clay suspension.

Because of the unstable nature of the treated clay suspensions, all clay suspensions were periodically reprocessed to eliminate free electrolytes and to keep the clay suspensions in monoionic forms.

4.2. Determination of the Cation Exchange Capacities

A method based on an actual exchange of the counter ion Sr^{++} and the radioisotope Sr^{85++} was employed to determine the exchange capacities. The exchange capacities were determined as a function of Sr^{++} concentration varying from 1×10^{-4} to 1×10^{-2} N. The experimental results are presented in Fig. 3. It is shown in Equation (3-2) that the slopes of the curves in Fig. 3 represent the exchange capacities.

TABLE 4
MEASUREMENT OF CONDUCTIVITY AND pH OF CLAY MINERAL SUSPENSIONS

Clay	Aging = 0 month		Aging = 1 month		Aging = 2 months	
	Conductivity μ mols/cm	pH	Conductivity μ mols/cm	pH	Conductivity μ mols/cm	pH
Sr-Montmorillonite	3.0	6.3	8.8	6.1	9.6	6.2
Sr-Illite	9.0	6.0	65.0	5.8	73.0	5.9
Ca-Montmorillonite	3.0	6.0	9.5	5.7	10.0	6.0
Ca-Illite	18.5	6.3	66.0	6.1	69.0	6.1
Na-Montmorillonite	9.0	7.8	18.5	7.4	20.5	7.2
Na-Illite	16.0	7.6	110.5	7.2	130.0	7.2
Demineralized water	0.7	6.3				

	Clay	Grinding	Slope(C.E.C.)
a	Montmorillonite	1-2 hr	0.690 m.eq./gr
b	Illite	2 hr	0.203 m.eq./gr
c	Illite	1 hr	0.177 m.eq./gr

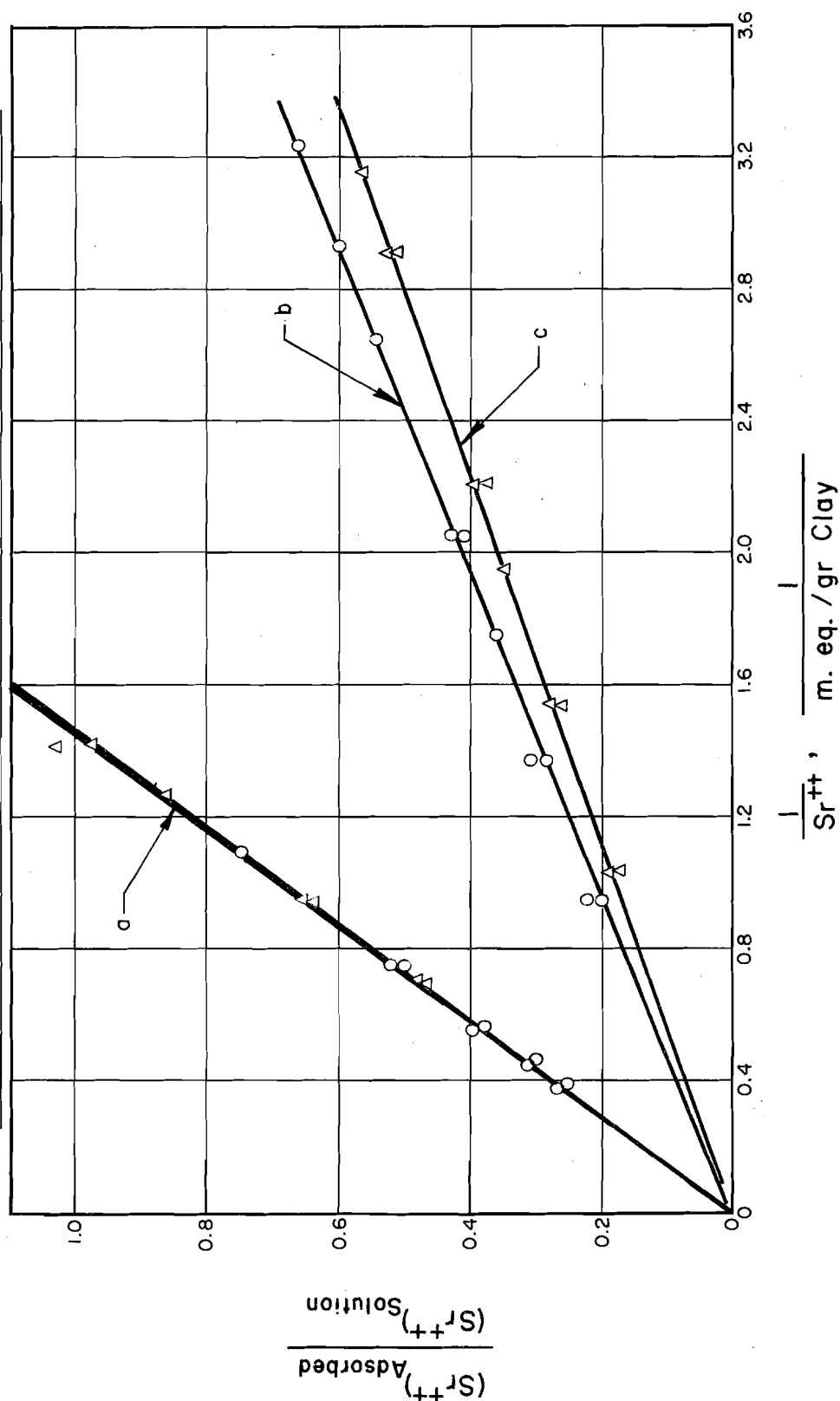


FIG. 3 ION EXCHANGE CAPACITY OF CLAY MINERALS AS A FUNCTION OF THE COUNTER ION CONCENTRATION.

It is apparent from the curves shown in Fig. 3 that the values of the exchange capacities do not change in the range of Sr^{++} concentration used. In the case of the illite minerals, two batches prepared separately showed different values for the capacities. This probably resulted from the fact that the illite minerals which had been subjected to more steps of the centrifuge-resuspension cycles during the treatment process might have been broken down to finer particles by the high speed rotary blade of the suspension equipment. The dependence of illite exchange capacity on its particle size was also reported by Grim⁽¹³⁾.

For comparison, the exchange capacities were also determined by the ammonium acetate method and the methylene blue method discussed in Section 3.2.2.1. The results are summarized in Table 5.

TABLE 5
EXCHANGE CAPACITIES OF CLAY MINERALS

Method	Montmorillonite		Illite	
	C.E.C. \pm s.d. m.eq./100 g	Sample number	C.E.C. \pm s.d. m.eq./100 g	Sample number
Sr^{++} exchange	69.0 \pm 1.9	20	17.7 \pm 0.64	20
Ammonium acetate	71.0 \pm 2.5	12	18.1 \pm 1.1	12
Methylene blue	75.2 \pm 2.3	12	22.5 \pm 1.3	12

A fair agreement was observed between the ammonium acetate method and the Sr^{++} exchange method. However, the exchange capacity determined by methylene blue adsorption was generally 10 to 20% greater than those of the other methods. This probably is due to the monoionic adsorption of methylene blue in addition to the ionic adsorption. There was also uncertainty in the ionic purity of methylene blue used (Fisher

Scientific Company). Higher results with the methylene blue method were also reported by Ludwig and his co-workers⁽³⁹⁾.

4.3. Behavior of Hydrogen Ions in Clay Ion-Exchange Reactions

The study of the behavior of hydrogen ions was conducted because of necessity for determining whether hydrogen ions can be treated as an independent competing counter ion or whether the hydrogen ion seriously influences the exchange parameters by some mechanism other than itself competing for the exchange site. The effects of hydrogen ions on soil ion-exchange reactions were examined in terms of: (1) the equivalence of the exchange of strontium by hydrogen, (2) the soil selectivity of hydrogen ions in reference to strontium ions, and (3) the effects of adsorbed hydrogen ions on the selectivities of soil exchangers for other counter ion pairs $\text{Sr}^{++}\text{-Mg}^{++}$ and $\text{Sr}^{++}\text{-Ca}^{++}$.

The equivalence of the hydrogen exchange was investigated by adding known amounts of H^+ ions into the system in which Sr-clay minerals were in equilibrium with known amounts of Sr^{++} ions. Increases in the amounts of Sr^{++} ions in the solution phase (eluted Sr^{++}) as H^+ ions were added were computed from Equation (3-6). In order to investigate the behavior of hydrogen ions on the clay exchanger phase, in another batch containing the same amounts of Sr-clay and Sr^{++} , OH^- ions were added, and the change in Sr^{++} concentration in the solution phase was measured as a function of disappeared hydroxide (ΔOH^-) in the solution phase. The experimental results are presented in Fig. 4, in which the eluted Sr^{++} from Sr-clay minerals were plotted as a function of disappeared hydrogen (ΔH^+).

	Sr^{++} added	H^+ added	OH^- added	Clay added	pH
a	4×10^{-4}	$0-4 \times 10^{-4}$	$0-1.6 \times 10^{-4}$	Sr-Mont. $= 1.0 \times 10^{-3}$	3.73-7.45
b	2×10^{-4}	$0-4 \times 10^{-4}$	$0-1.6 \times 10^{-4}$	Sr-Ill. $= 4.4 \times 10^{-4}$	4.10-7.30

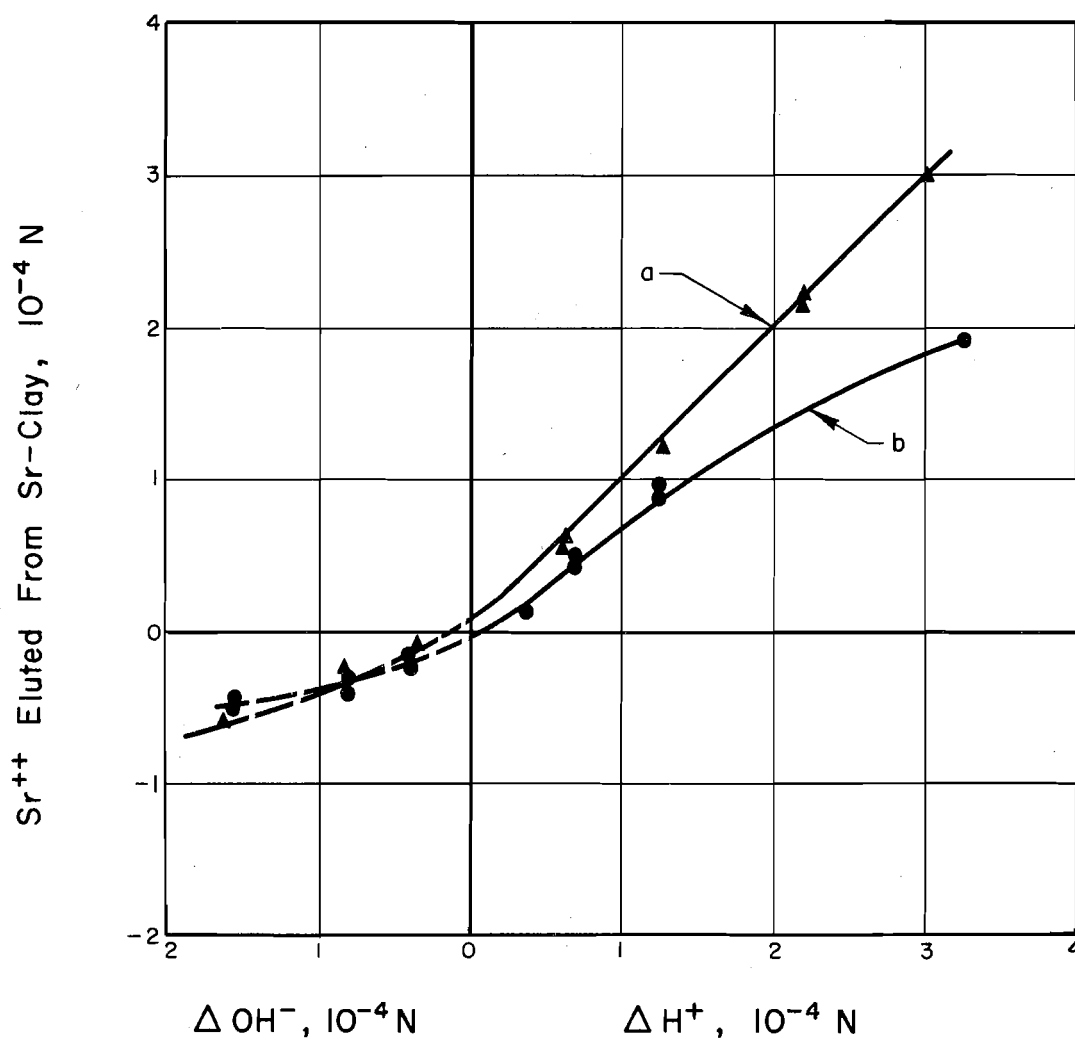


FIG. 4 EFFECTS OF H^+ AND OH^- IONS ON EXCHANGE CAPACITY OF CLAY MINERALS.

A line with the slope of unity and passing through the origin in Fig. 4 would represent the equivalence of the exchange of strontium by hydrogen. The curves in Fig. 4 are further extended to represent the eluted Sr^{++} as a function of ΔOH^- (dotted lines). The negative quantities of the eluted Sr^{++} correspond to the increased amounts of Sr^{++} adsorbed on the clay minerals. The origin in Fig. 4 represents the system containing Sr-clay and Sr^{++} ions before either H^+ or OH^- are added to the system. The pH values before either H^+ or OH^- were added were 6.5 and 6.7 for the systems containing Sr-montmorillonite and Sr-illite, respectively.

On the basis of the experimental data, it is apparent that the reaction of hydrogen ions does not always involve ion exchange. That hydrogen ions may involve a reaction other than ion exchange is shown by the fact that the equivalence of the disappeared hydrogen ions and eluted Sr^{++} was not observed at the pH higher than 6.5 for montmorillonite and not at all for illite. The equivalence of the disappeared hydrogen and eluted Sr^{++} from Sr-clay minerals was only observed in montmorillonite at a pH value lower than 6.5. In the case of illite minerals, the disappeared hydrogen ions (ΔH^+) were more than equivalent amounts of Sr^{++} eluted. The excess amounts of hydrogen may have been involved in attacking the clay structure or its impurity. Increase in the amounts of Sr^{++} adsorption, that is the amounts disappeared from the solution phase, by addition of OH^- ions was observed in both montmorillonite and illite, which indicates that either creation of new exchange sites or the precipitation of Sr^{++} may have occurred. The solubility of $\text{Sr}(\text{OH})_2$ at the highest pH (7.4) indicates precipitation is not expected. It was more

probable that the addition of OH^- created new exchange sites on which Sr^{++} could be adsorbed. The creation of new exchange sites perhaps resulted from the fact that OH^- ions might have neutralized hydrogens on the clay minerals, and hence created new exchange sites for the adsorption of Sr^{++} . The hydrogen neutralized by OH^- ions might be either the hydrogen of exposed hydroxyl parts of the clay structure or the hydrogens adsorbed on the clay minerals during their treatment process. The possible creation of exchange sites by removing the hydrogen of exposed hydroxyl groups of clay minerals was reported by Grim⁽¹³⁾.

The selectivity of hydrogen with respect to strontium ion was examined by determining the equilibrium constant (K_{SrH}) for the ion-exchange reaction between hydrogen and strontium. The results are summarized in Table 6. The selectivity of montmorillonite for hydrogen

TABLE 6

EQUILIBRIUM CONSTANT OF MONTMORILLONITE
FOR THE EXCHANGE BETWEEN Sr^{++} AND H^+

pH	K_{SrH}	\bar{m}_{H}
		$\bar{m}_{\text{H}} + \bar{m}_{\text{Sr}}$
4.9	0.085	0.065
4.5	0.110	0.130
3.7	0.800	0.220

decreased as more hydrogen adsorbed on montmorillonite, indicating the decrease in the affinity for H^+ as more H^+ occupied the exchange sites. The change in the selectivity probably resulted from the fact that the exchange sites are not uniform in their properties. Initially, the

hydrogen ions might be adsorbed on more favorable sites resulting in its high affinity. As more hydrogen occupied the favorable sites, further adsorption of hydrogen may have involved unfavorable sites, resulting in the low value of the selectivity.

The determination of equilibrium constants for the counter ion pairs $\text{Sr}^{++}\text{-Ca}^{++}$ and $\text{Sr}^{++}\text{-Mg}^{++}$ in the presence of hydrogen ions in the exchanger phase are summarized in Table 7. As shown in Table 7, the equilibrium constants for the ion pairs $\text{Sr}^{++}\text{-Ca}^{++}$ and $\text{Sr}^{++}\text{-Mg}^{++}$ are independent of the presence of hydrogen ions in the exchanger phase, even

TABLE 7
INFLUENCE OF HYDROGEN ON THE EXCHANGE EQUILIBRIUM
CONSTANTS OF MONTMORILLONITE

K_o Sr-Mg	% exchange sites covered by H^+	Final pH	K_o Sr-Ca	% exchange sites covered by H^+	Final pH
1.31	3.35	5.35	1.09	3.25	5.14
1.30	6.23	4.79	1.07	6.25	4.76
1.22	12.2	4.40	1.03	12.2	4.42
1.31	18.9	3.70	1.10	21.0	3.76

though the equilibrium constants for the reaction between hydrogen and others depended on the hydrogen concentration. Thus, it can be concluded that regardless of the types of exchange sites on a clay mineral or the presence of other cations, the selectivity coefficient of a clay mineral is constant for most of the counter ion pairs except that involving hydrogen ions.

4.4. Determination of Equilibrium Constants

A number of ion-exchange expressions discussed in Section 2.3.1 were subjected to experimental tests. The experiments were performed to determine the equilibrium constants for various counter ion pairs, $\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$, and $\text{Sr}^{++}\text{-Na}^+$, over a wide range of concentrations. The equilibrium constants were computed from expressions described in Section 2.3.1. Rearranging the terms of Equation (2-16) and taking logarithms leads to the equation,

$$\log \frac{(\bar{a}_A)^b}{(\bar{a}_B)^a} = \log \frac{(a_A)^b}{(a_B)^a} + \log K \quad (4-1a)$$

or

$$\log \frac{(\bar{m}_A)^b}{(\bar{m}_B)^a} \frac{(\bar{\gamma}_A)^b}{(\bar{\gamma}_B)^a} = \log \frac{(m_A)^b}{(m_B)^a} \cdot \frac{(\gamma_A)^b}{(\gamma_B)^a} + \log K, \quad (4-1b)$$

which indicates that if the activity ratios $(\bar{m}_A)^b (\bar{\gamma}_A)^b / (\bar{m}_B)^a (\bar{\gamma}_B)^a$ and $(m_A)^b (\gamma_A)^b / (m_B)^a (\gamma_B)^a$ were to be plotted on log-log scale, the form of Equation (2-16) would be a straight line whose slope is unity, and the intercept on the ordinate (1.0 on log scale) is the equilibrium constant.

The activity ratio in the exchanger phase $(\bar{a}_A)^b / (\bar{a}_B)^a$ was computed from the expressions proposed by Vanselow (Equation 2-20), and Krishnamoorthy and Overstreet (Equation 2-21). In the case of the ion pair with the same valence, the activity ratio reduces to $(\bar{m}_A)^b / (\bar{m}_B)^a$ for both expressions.

Three different values of the solution activity ratio were used: (a) $(a_A)^b / (a_B)^a = (m_A)^b / (m_B)^a$, (b) $(a_A)^b / (a_B)^a =$

$(m_A)^b (\gamma_A)^b / (m_B)^a (\gamma_B)^a$ with $(\gamma_A)^b / (\gamma_B)^a$ computed using the individual ionic concentration, and (c) $(a_A)^b / (a_B)^a = (m_A)^b (\gamma_A)^b / (m_B)^a (\gamma_B)^a$ with $(\gamma_A)^b / (\gamma_B)^a$ computed using the total ionic concentration. In the case of the ion pair of the same valence, (a) and (c) reduce to the same value.

The reliability of each expression was tested by examining the ability of each expression to produce a constant value of the equilibrium constant over the range of concentrations used.

Each equilibrium reaction was carried out over a wide range of the counter ion concentrations as shown in Tables 8 and 9. The equilibrium constants at each concentration were computed from the expressions discussed in Section 2.3.1. The average values for each reaction and the experimental conditions are summarized in Tables 8 and 9.

Using the average value of the equilibrium constants, a straight line satisfying the equilibrium condition is drawn on a log-log plot (Fig. 5 through Fig. 12). On each of the same figures, the experimental data in terms of the exchanger activity ratio $(\bar{m}_A)^b (\bar{\gamma}_A)^b / (\bar{m}_B)^a (\bar{\gamma}_B)^a$ are plotted as a function of the solution activity ratio $(m_A)^b (\gamma_A)^b / (m_B)^a (\gamma_B)^a$. By comparing the experimental points with the line representing the average value of the experimental points, one can examine qualitatively the degree and nature of the deviation of each experimental result.

In Figs. 5 and 6, the experimental results of the exchange reaction between Sr^{++} and Ca^{++} with montmorillonite and illite are shown. Because both cations have the same valence, the activity coefficient ratio in the exchanger phase is unity. In both Figs. 5 and 6, the curve (a) on the left represents the value without the solution phase activity correction. The results are present similarly in Figs. 7 and 8 for the reaction between Sr^{++} and Mg^{++} .

TABLE 8
THE VALUE OF EQUILIBRIUM CONSTANTS FOR THE EXCHANGE
BETWEEN $\text{Sr}^{++}\text{-Ca}^{++}$ AND $\text{Sr}^{++}\text{-Mg}^{++}$

Clay	Concentrations, N		$K_{AB} \pm \text{s.d.}$	$K_{AB} \pm \text{s.d.}$
	A^{a+}	B^{b+}	Coefficient of Variation, C_v	Coefficient of Variation, C_v
Sr-Mont.	Sr^{++}	Ca^{++}	1.065 ± 0.085	1.026 ± 0.143
5-10x10 ⁻⁴	5×10^{-6} - 2×10^{-3}	1×10^{-4} - 2×10^{-3}	8.0	14.0
Ca-Mont.	Sr^{++}	Ca^{++}	1.086 ± 0.045	0.8853 ± 0.110
5-10x10 ⁻⁴	5×10^{-6} - 2×10^{-3}	1×10^{-4} - 2×10^{-3}	4.2	12.5
Sr-Illite	Sr^{++}	Ca^{++}	1.110 ± 0.080	1.067 ± 0.105
5-20x10 ⁻⁴	5×10^{-6} - 1×10^{-3}	1×10^{-4} - 1×10^{-3}	7.2	9.8
Ca-Illite	Sr^{++}	Ca^{++}	1.116 ± 0.068	0.9449 ± 0.091
5-20x10 ⁻⁴	5×10^{-6} - 1×10^{-3}	1×10^{-4} - 1×10^{-3}	5.8	9.6
Sr-Mont.	Sr^{++}	Mg^{++}	1.262 ± 0.094	1.220 ± 0.120
5-10x10 ⁻⁴	1×10^{-4} - 1×10^{-3}	1×10^{-4} - 5×10^{-3}	7.5	9.8
Mg-Mont.	Sr^{++}	Mg^{++}	1.293 ± 0.083	0.920 ± 0.168
5-10x10 ⁻⁴	1×10^{-5} - 1×10^{-3}	1×10^{-4} - 5×10^{-3}	6.4	18.4
Sr-Illite	Sr^{++}	Mg^{++}	1.493 ± 0.067	1.358 ± 0.129
5-20x10 ⁻⁴	1×10^{-5} - 1×10^{-3}	1×10^{-4} - 1×10^{-3}	4.5	9.5
Mg-Illite	Sr^{++}	Mg^{++}	1.619 ± 0.099	1.348 ± 0.087
5-2-x10 ⁻⁴	1×10^{-5} - 1×10^{-3}	1×10^{-4} - 1×10^{-3}	6.1	6.5

TABLE 9

THE VALUE OF EQUILIBRIUM CONSTANTS FOR THE EXCHANGE BETWEEN Na^+ AND Sr^{++}
(K1 and K2 are computed with individual and total ionic strengths, respectively)

Concentrations, N	K_{NaSr}	\pm s.d.	K_{NaSr}	\pm s.d.	K_{NaSr}^V	\pm s.d.	K_{NaSr}^K	\pm s.d.
Sr-Mont. = $5 \cdot 10 \times 10^{-4}$	8.523×10^{-4}	$\pm 1.53 \times 10^{-4}$	$K1 = 1.126 \times 10^{-3}$	$\pm 2.88 \times 10^{-4}$	$K1 = 1.294 \pm 0.252$		$K1 = 1.053 \pm 0.273$	
$\text{Na}^+ = 1 \cdot 50 \times 10^{-3}$								
$\text{Sr}^{++} = 1 \cdot 200 \times 10^{-5}$			$K2 = 6.804 \times 10^{-4}$	$\pm 1.33 \times 10^{-4}$	$K2 = 0.7852 \pm 0.156$		$K2 = 0.6148 \pm 0.160$	
Na-Mont. = $5 \cdot 10 \times 10^{-4}$	8.380×10^{-4}	$\pm 1.27 \times 10^{-4}$	$K1 = 1.190 \times 10^{-3}$	$\pm 1.66 \times 10^{-4}$	$K1 = 1.2187 \pm 0.189$		$K1 = 1.261 \pm 0.276$	
$\text{Na}^+ = 1 \cdot 5 \times 10^{-2}$								
$\text{Sr}^{++} = 1 \cdot 20 \times 10^{-4}$			$K2 = 6.970 \times 10^{-4}$	$\pm 1.63 \times 10^{-4}$	$K2 = 0.6944 \pm 0.056$		$K2 = 0.6356 \pm 0.161$	
Sr-Illite = $5 \cdot 20 \times 10^{-4}$	2.701×10^{-4}	$\pm 2.33 \times 10^{-5}$	$K1 = 3.782 \times 10^{-4}$	$\pm 6.88 \times 10^{-5}$	$K1 = 0.7455 \pm 0.084$		$K1 = 1.053 \pm 0.245$	
$\text{Na}^+ = 5 \cdot 20 \times 10^{-3}$								
$\text{Sr}^{++} = 5 \cdot 100 \times 10^{-5}$			$K2 = 2.010 \times 10^{-4}$	$\pm 2.10 \times 10^{-5}$	$K2 = 0.5146 \pm 0.049$		$K2 = 0.7033 \pm 0.192$	
Na-Illite = $5 \cdot 20 \times 10^{-4}$	3.024×10^{-4}	$\pm 4.20 \times 10^{-5}$	$K1 = 3.883 \times 10^{-4}$	$\pm 4.20 \times 10^{-5}$	$K1 = 0.8327 \pm 0.129$		$K1 = 1.179 \pm 0.159$	
$\text{Na}^+ = 5 \cdot 20 \times 10^{-3}$								
$\text{Sr}^{++} = 1 \cdot 10 \times 10^{-4}$			$K2 = 2.192 \times 10^{-4}$	$\pm 1.90 \times 10^{-5}$	$K2 = 0.5258 \pm 0.092$		$K2 = 0.5472 \pm 0.097$	

— average value

o ▲ experimental data

a: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Ca}}} = 1.0$; $Ko_{\text{SrCa}} = 1.0855$

b: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Ca}}} = \text{computed with individual ionic strength}$; $Ko'_{\text{SrCa}} = 0.8853$

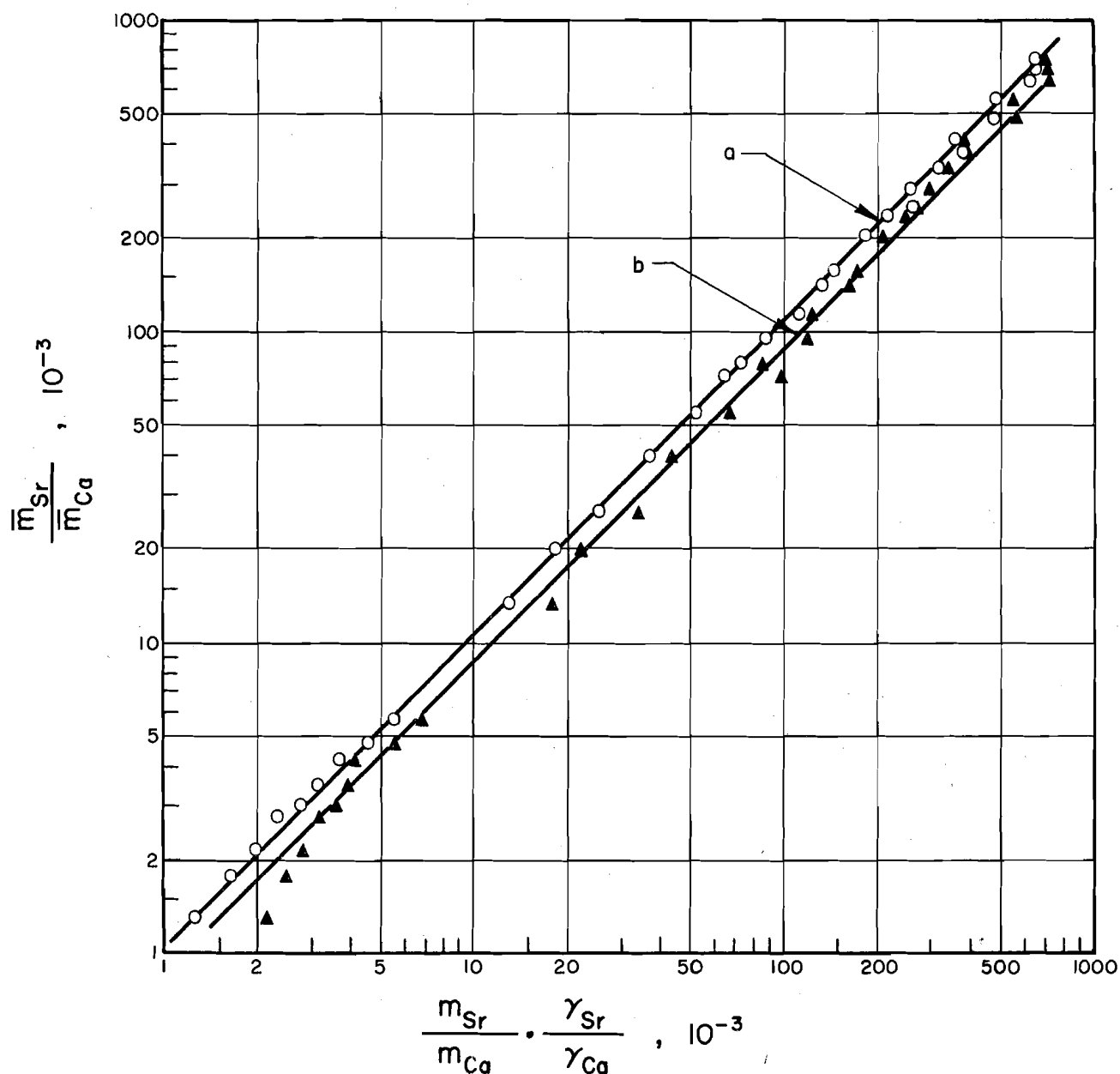


FIG. 5 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH MONTMORILLONITE, Ca^{++} , AND Sr^{++} .

— average value

o Δ experimental data

73

a: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Ca}}} = 1.0; K_{\text{SrCa}} = 1.1162$

b: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Ca}}} = \text{computed with individual ionic strength}; K'_{\text{SrCa}} = 0.9449$

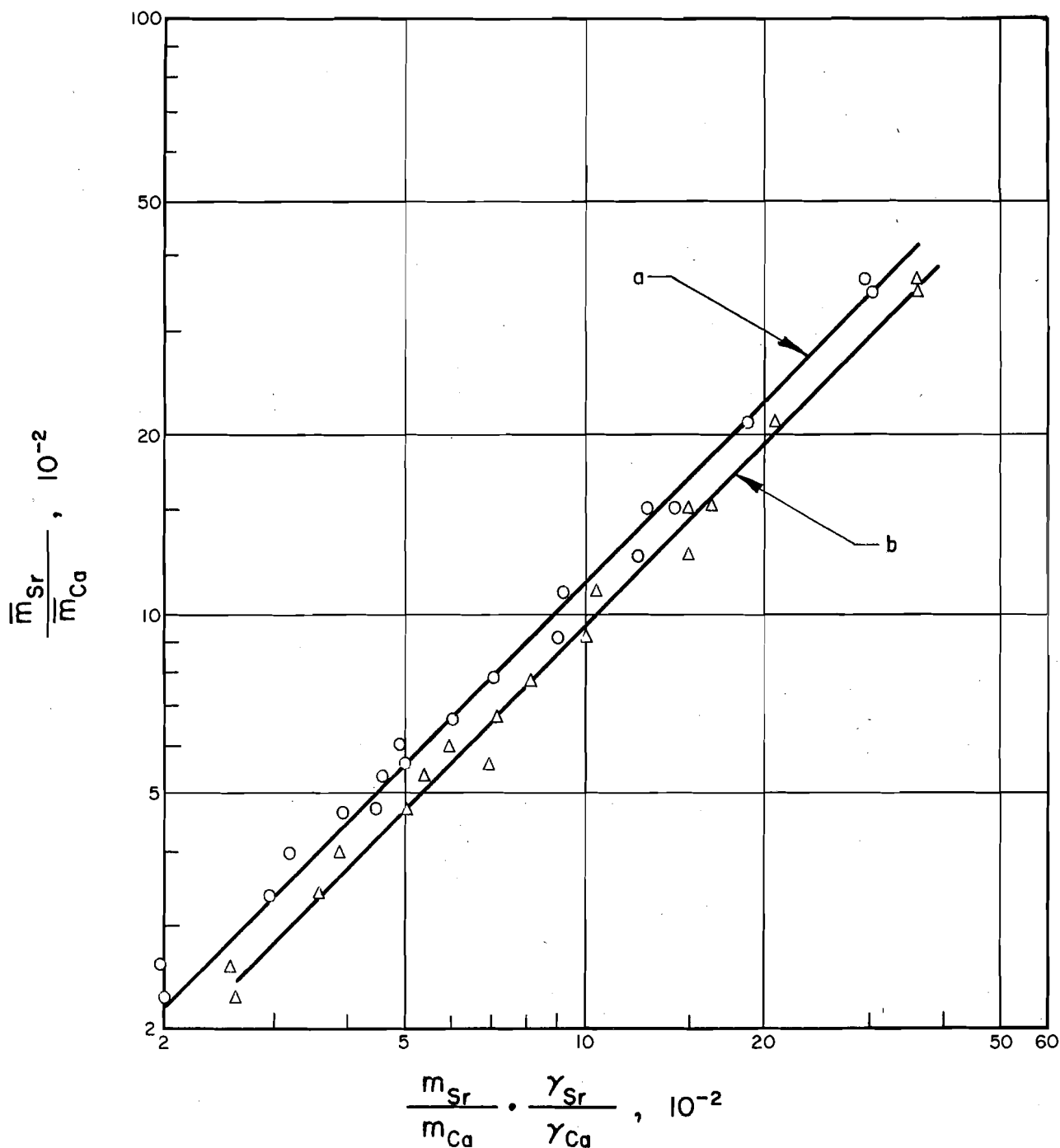


FIG. 6 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH ILLITE, Sr^{++} , AND Ca^{++} .

— average value

o Δ experimental data

a: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Mg}}} = 1.0$; $Ko_{\text{SrMg}} = 1.293$

b: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Mg}}} = \text{computed with individual ionic strength}$; $Ko'_{\text{SrMg}} = 0.92$

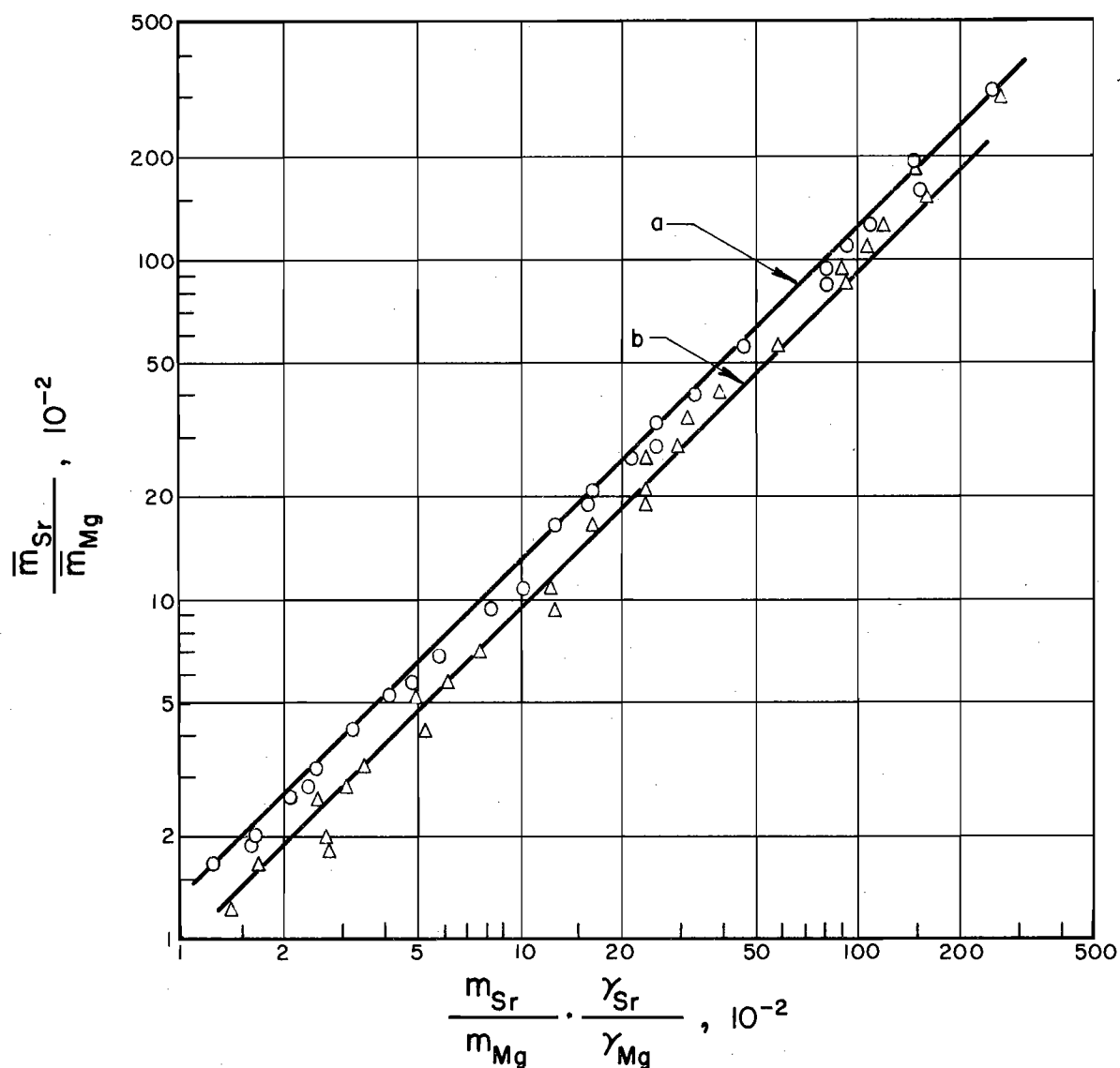


FIG. 7 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH MONTMORILLONITE, Mg^{++} , AND Sr^{++} .

— average value

o Δ experimental data

a: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Mg}}} = 1.0; K_{\text{SrMg}} = 1.619$

b: $\frac{\gamma_{\text{Sr}}}{\gamma_{\text{Mg}}} = \text{computed with individual ionic strength}; K'_{\text{SrMg}} = 1.348$

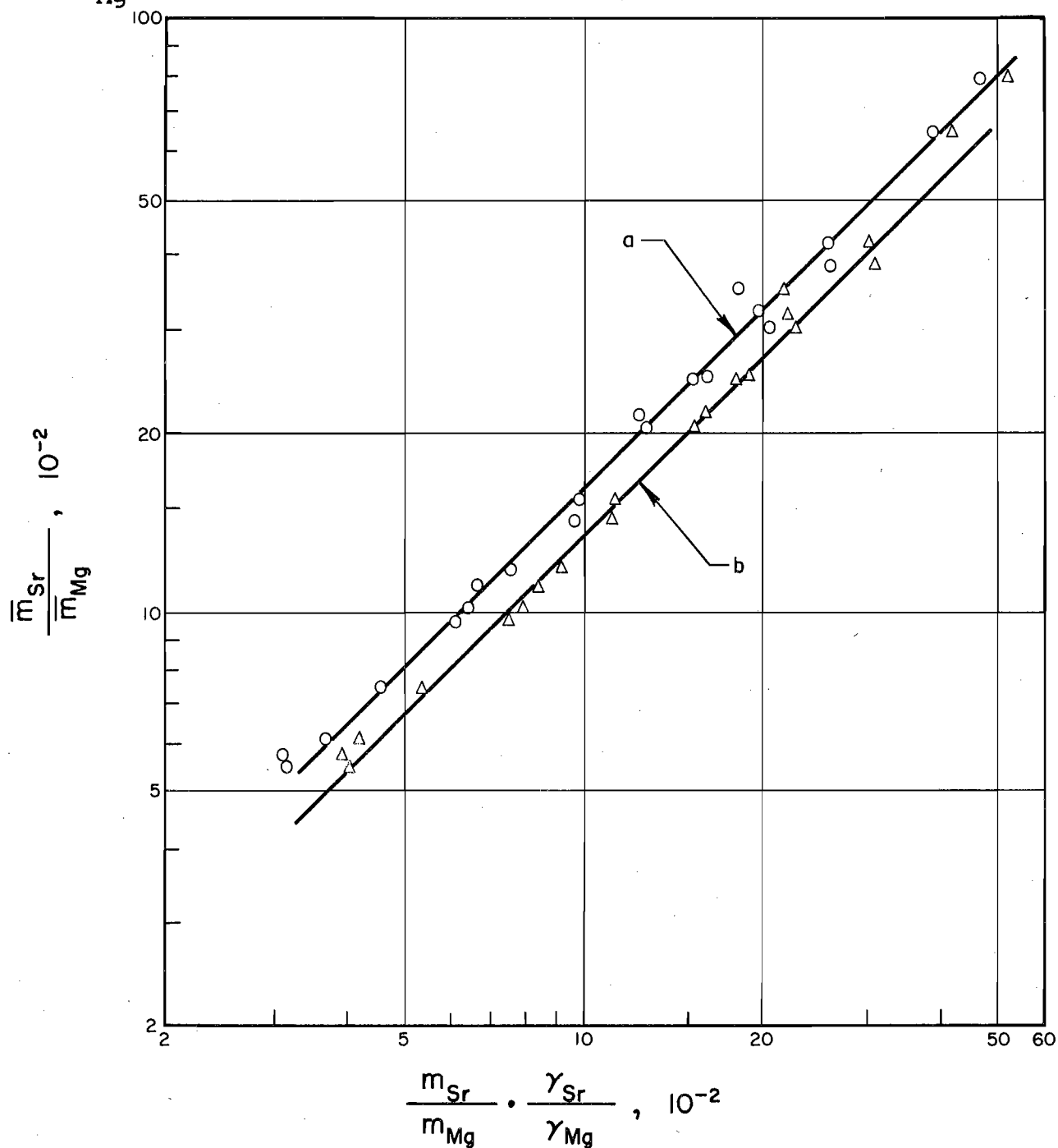


FIG. 8 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH ILLITE, Sr^{++} , AND Mg^{++} .

— average value

76

o Δ □ experimental data

a: $\frac{\gamma_{Na}}{\gamma_{Sr}} = 1.0; K_{o_{NaSr}} = 8.3803 \times 10^{-4}$

b: $\frac{\gamma_{Na}}{\gamma_{Sr}} = \text{computed with individual ionic strength}; K_{o_{NaSr}} = 1.1897 \times 10^{-3}$

c: $\frac{\gamma_{Na}}{\gamma_{Sr}} = \text{computed with total ionic strength}; K_{o_{NaSr}} = 6.9695 \times 10^{-4}$

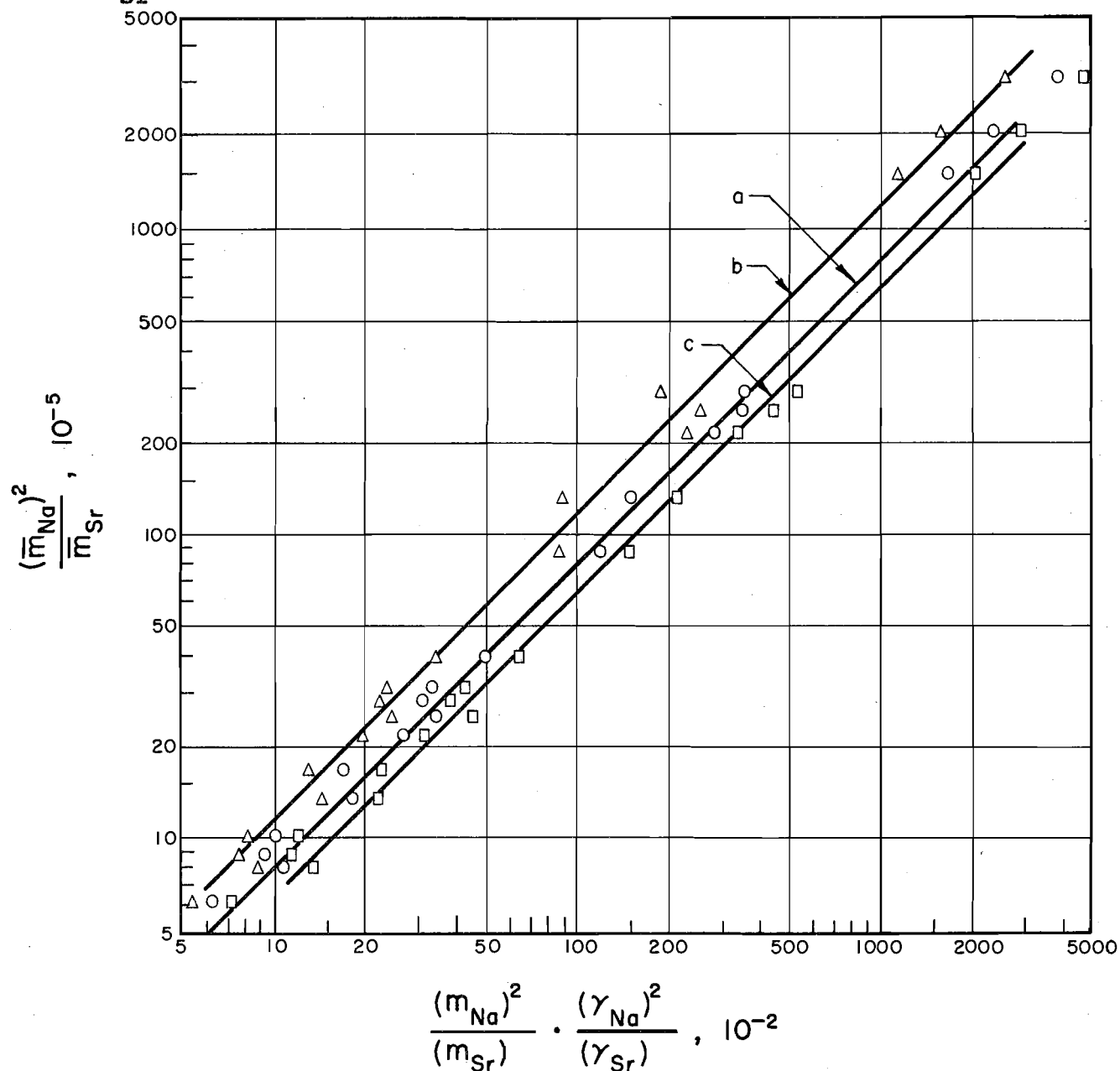


FIG. 9 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH MONTMORILLONITE, Na⁺, AND Sr⁺⁺.

— average value
 o Δ □ experimental data

a: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = 1.0; K_{\text{NaSr}}^k = 8.000 \times 10^{-1}$

b: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = \text{computed with individual ionic strength}; K_{\text{NaSr}}^k = 1.261$

c: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = \text{computed with total ionic strength}; K_{\text{NaSr}}^k = 6.356 \times 10^{-1}$

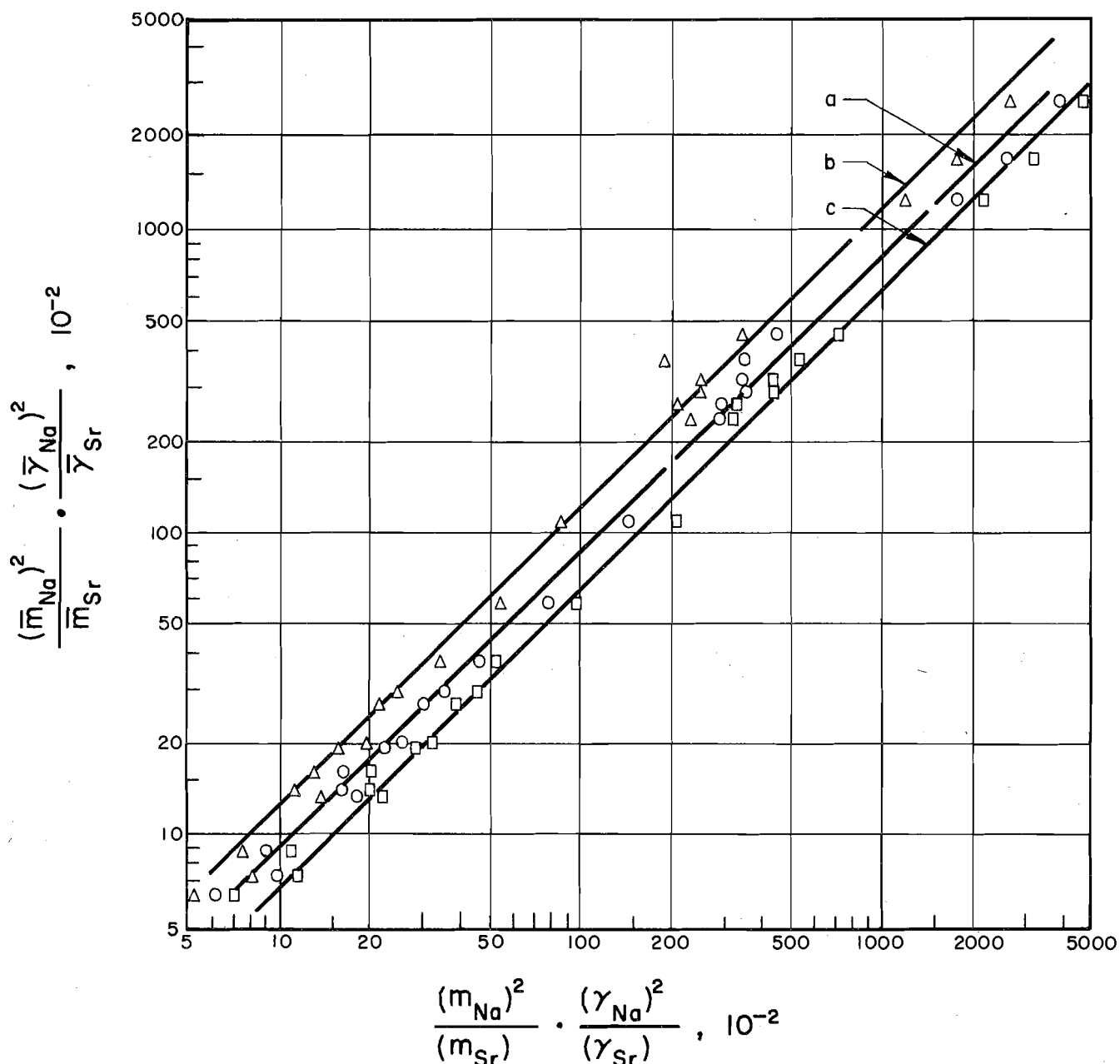


FIG. 10 CORRECTED EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH MONTMORILLONITE, Na^+ , AND Sr^{++} .

— average value
 o Δ □ experimental data

a: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = 1.0; K_{\text{NaSr}} = 3.0241 \times 10^{-4}$

b: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = \text{computed with individual ionic strength}; K_{\text{NaSr}}' = 3.8826 \times 10^{-4}$

c: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = \text{computed with total ionic strength}; K_{\text{NaSr}}' = 2.192 \times 10^{-4}$

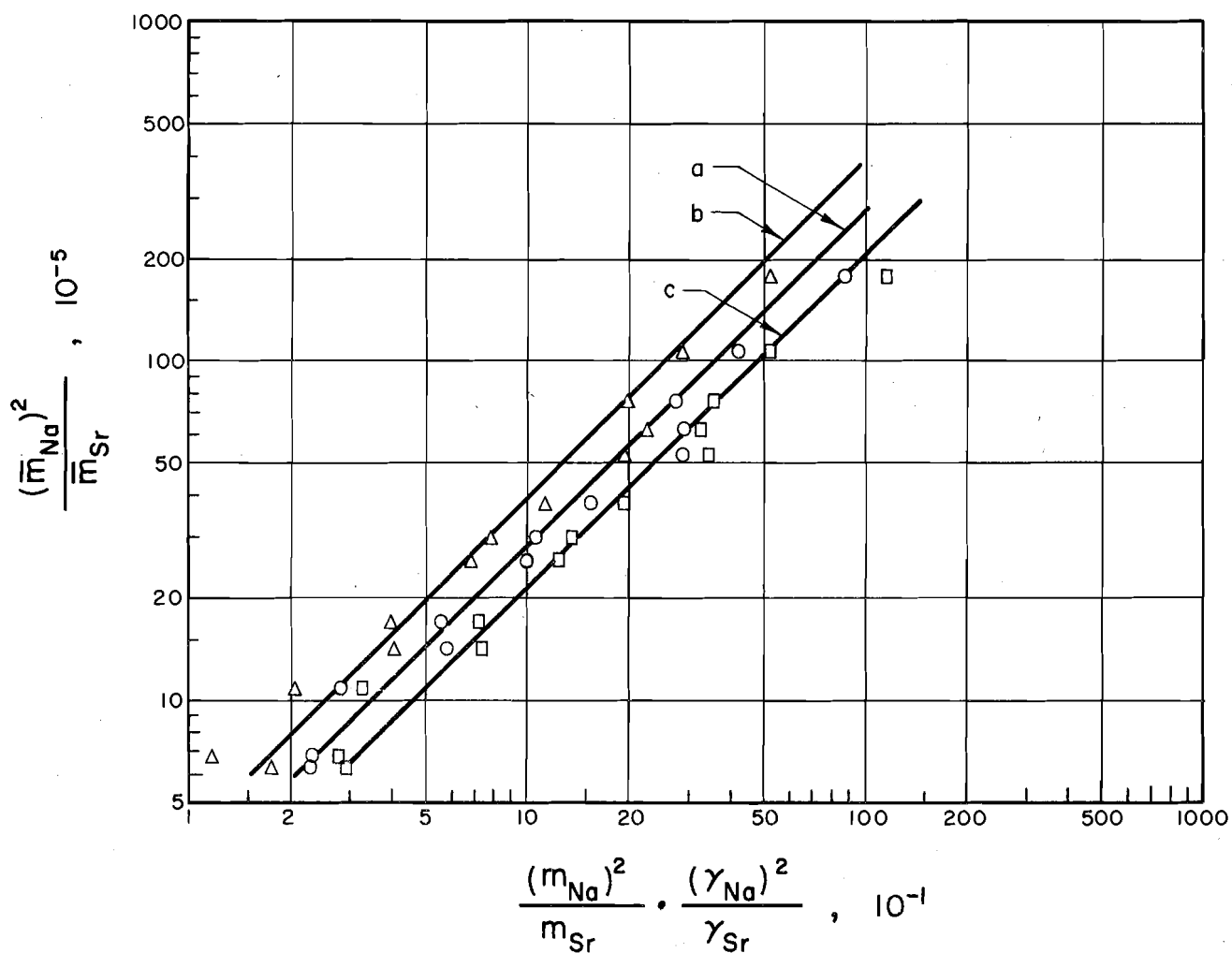


FIG. II EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH ILLITE, Na^+ , AND Sr^{++} .

— average value
 o Δ □ experimental data

a: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = 1.0$; $K_{\text{NaSr}}^k = 7.000 \times 10^{-1}$

b: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = \text{computed with individual ionic strength}$; $K_{\text{NaSr}}^k = 1.179$

c: $\frac{\gamma_{\text{Na}}}{\gamma_{\text{Sr}}} = \text{computed with total ionic strength}$; $K_{\text{NaSr}}^k = 5.472 \times 10^{-1}$

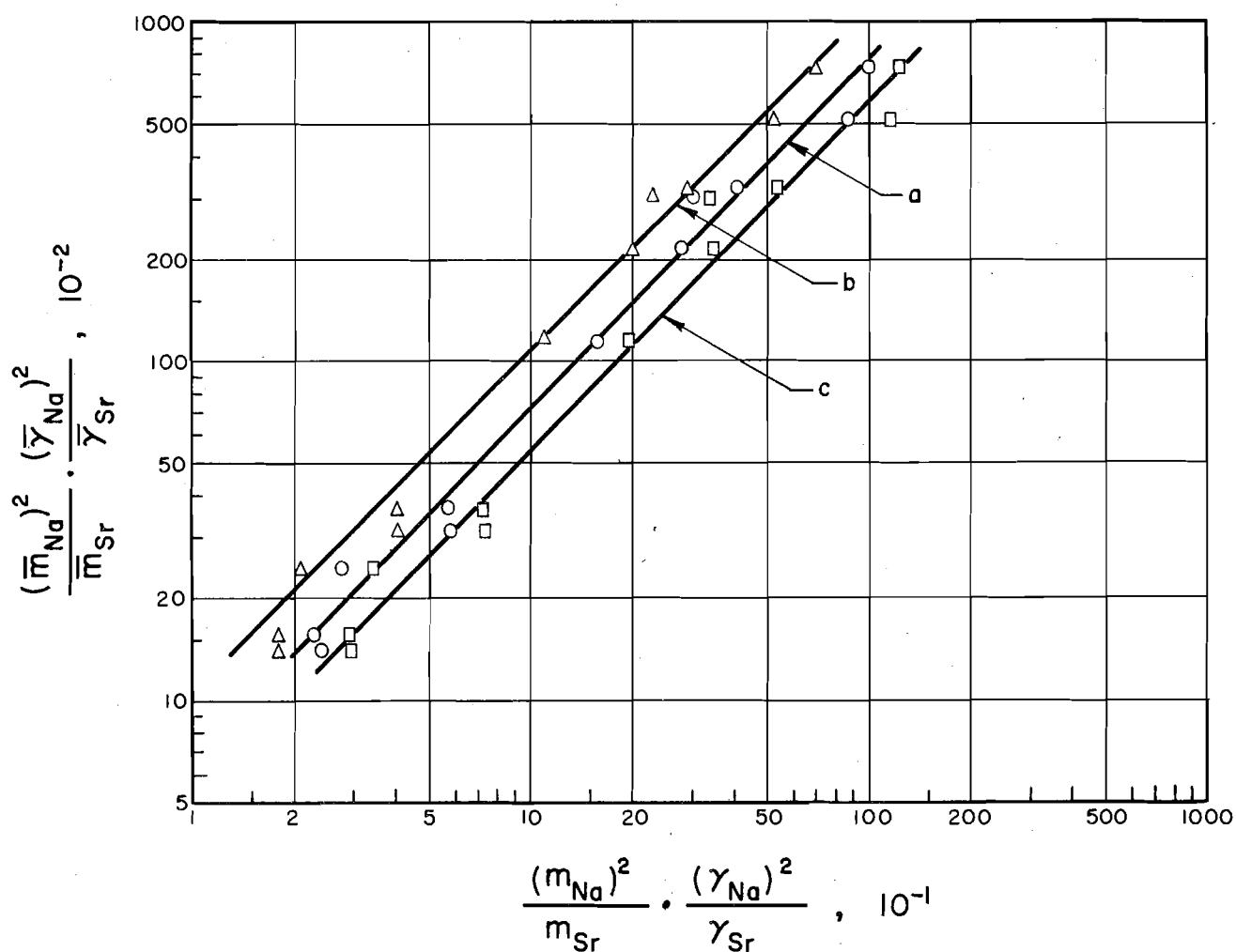


FIG. 12. CORRECTED EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH ILLITE, Na^+ , AND Sr^{++} .

In Figs. 9 and 10, the experimental results for the $\text{Sr}^{++}\text{-Na}^+$ exchange reaction with montmorillonite are presented. In Fig. 9, the concentration ratios in the exchanger phase are plotted as a function of the activity ratios in the solution phase. In Fig. 10, the activity ratios of the exchanger phase computed from Krishnamoorthy and Overstreet's expression (Equation 2-21) are plotted as a function of the activity ratios in the solution phase. Similarly, in Figs. 11 and 12, the experimental results with illite are presented.

It is apparent from the curves shown in Fig. 5 through Fig. 12 that regardless of the form of the expressions used for the computation of the equilibrium constant, they all show the same degree of reliability for producing a constant value of the equilibrium constant. There is no clear evidence of one expression being better than the others in describing the equilibrium conditions. No improvement on the constancy of the equilibrium constants by including the solution phase activity correction is observed. The coefficients of variation, $C_v = (\text{s.d.})/(\text{average value}) \times 100$ (Table 8), show that the variation of the equilibrium constant with the solution phase activity correction is even greater than that without the correction. The greater variation of the equilibrium constant with the solution activity correction may be a result of the approximation made in the computation of the activity coefficients.

In the case of the exchange reaction between Sr^{++} and Na^+ , the values of the equilibrium constants with and without the solid phase activity correction differed by a factor of about 1000. The constancy of the equilibrium constants computed from the two expressions, that is one with the exchanger phase activity correction and the other without the correction, is about the same over a wide range of counter ion

concentrations. The ratio of the two constants remained the same at about 1000.

On the basis of the findings in this section, it is concluded that: (1) the ion-exchange equilibrium of the counter ion pairs, Sr^{++} - Ca^{++} , Sr^{++} - Mg^{++} , and Sr^{++} - Na^+ with either montmorillonite or illite can be described satisfactorily with the simple mass-action equation without the activity correction; (2) regardless of the direction of the approach, that is whether A^{a+} is replacing B^{b+} or B^{b+} replacing A^{a+} , a constant value of the equilibrium constant is obtained; and (3) the direct relationship⁽¹⁷⁾ between the expanding properties of an exchange medium and its selectivity does not apply for the exchange reactions of montmorillonite and illite.

4.5. Ion-Exchange Equilibria of Heterogeneous Clay Mixtures

On the basis of the theoretical considerations discussed in Section 2.4, it was shown that in the case of exchange media that are mixtures of two or more pure exchangers, the equilibrium constant would not be a constant but would depend on the mixture and the concentration of reactants.

With the mixture of montmorillonite (8.9×10^{-4}) and illite (3.8×10^{-4} N), the exchange reaction between Sr^{++} and Mg^{++} was studied with varying concentrations of Sr^{++} and Mg^{++} . The results are presented in Fig. 14. The experimental values of the effective equilibrium constant of the mixture (Equation 2-22) were compared with the value estimated from the theoretical equation (Equation 2-23). The exchange reactions between Na^+ and Sr^{++} were also studied with a mixture of

montmorillonite and illite with varying illite contents from zero to 100%. The results are presented in Fig. 13.

From the results, it is evident that equilibrium constants of the clay mixtures depended on both clay composition and ion concentration. However, the effect of ion concentration was insignificant compared to that of the clay composition. On the basis of the experimental results, it is shown that an approximate estimate can be made of the equilibrium constant of a montmorillonite and illite mixture by a simple linear interpolation between the equilibrium constants of the two pure components and their relative amounts in the mixture. That is, the effective equilibrium constant \overline{K}_{AB} can be approximated by,

$$\overline{K}_{AB} = x_m (K_{AB})_m + (1 - x_m) (K_{AB})_i \quad (4-2)$$

where x_m and $1 - x_m$ are the fractions (expressed in equivalents) of montmorillonite and illite, and $(K_{AB})_m$ and $(K_{AB})_i$ are the equilibrium constants of pure montmorillonite and illite.

4.6. Ion-Exchange Equilibrium in a Multicomponent System

The mass-action expression, without the activity corrections, which has been found satisfactory for describing the exchange reactions involving most pairs of counter ions, was subjected to experimental tests for its applicability in the multicomponent system containing Na^+ , Mg^{++} , Ca^{++} , and Sr^{++} .

With the known amount of each cation added into the system (m_{Ca}^0 , m_{Na}^0 , m_{Mg}^0 , and m_{Sr}^0) and the equilibrium constants determined in the

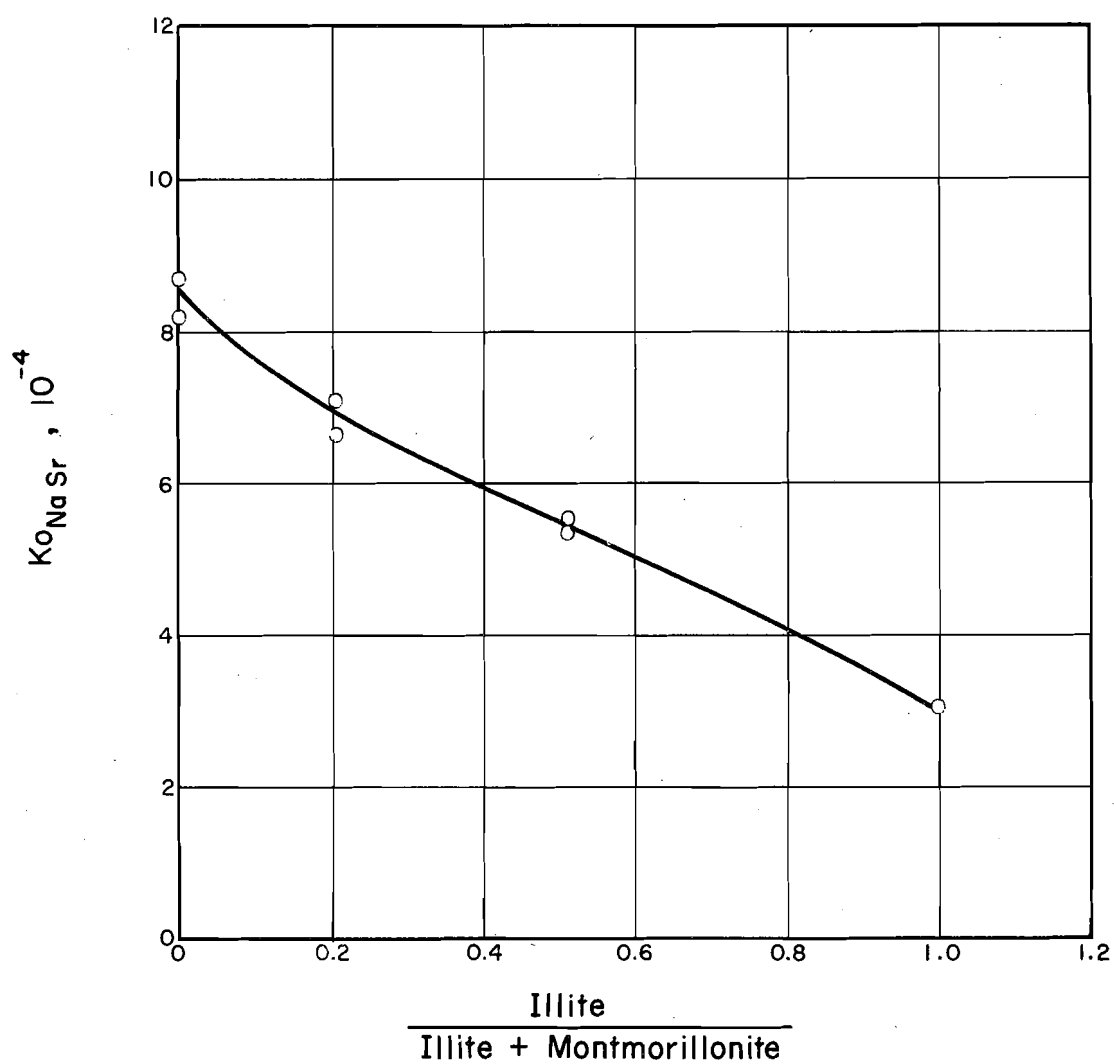


FIG. 13 EFFECTS OF IMPURITY OF CLAY ON EQUILIBRIUM DISTRIBUTION OF COUNTER IONS, Sr^{++} , AND Na^{+} .

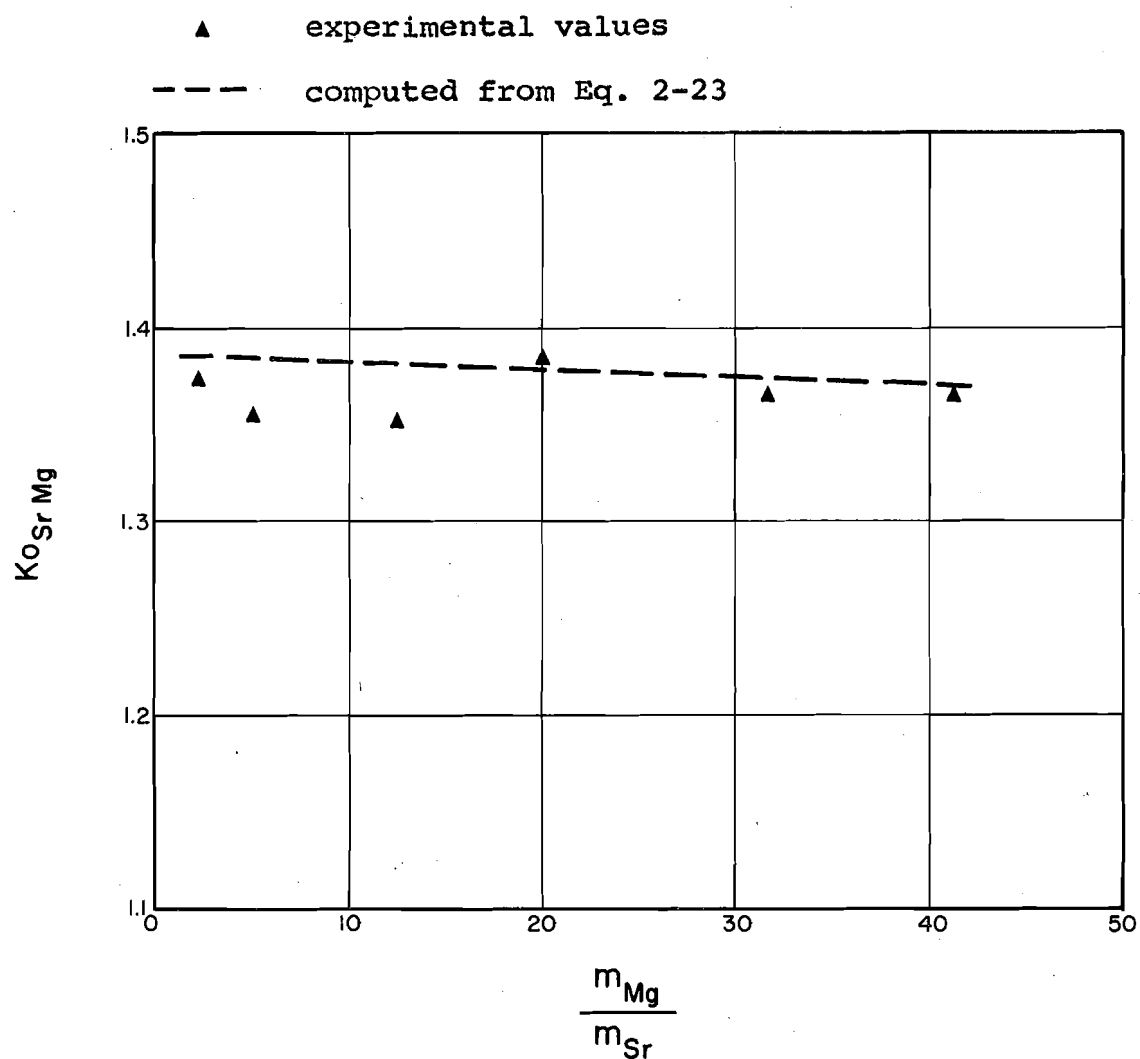


FIG. 14 EQUILIBRIUM CONSTANTS OF A CLAY MIXTURE AS A FUNCTION OF THE COUNTER ION CONCENTRATIONS.

previous section, the final Sr^{++} distributions were estimated using Equation (3-5), which was derived from a set of simultaneous mass-action expressions representing the reactions in the system. The estimated Sr^{++} distributions were compared with the experimental results. The results are presented in Figs. 15, 16, and 17. The experimental conditions are summarized in Table 10.

In Figs. 15, 16, and 17, the estimated values are presented as lines, while the points represent the experimental data. It is apparent from the curves and points shown in Figs. 15, 16, and 17 that the mass-action expression was quite satisfactory for describing the equilibrium conditions even in a multicomponent system.

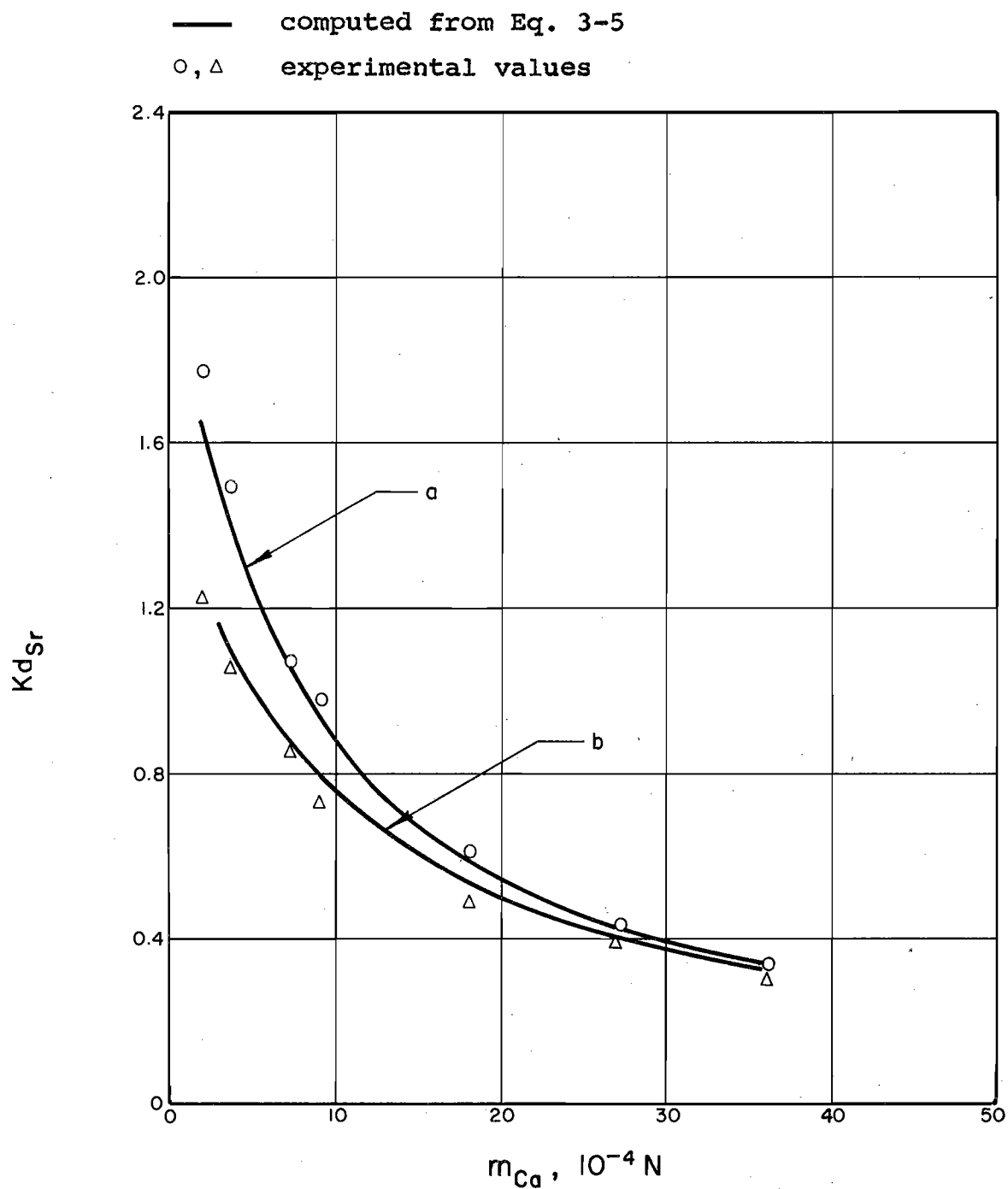


FIG. 15 ION EXCHANGE EQUILIBRIUM OF MONTMORILLONITE WITH THREE COMPETING COUNTER IONS.

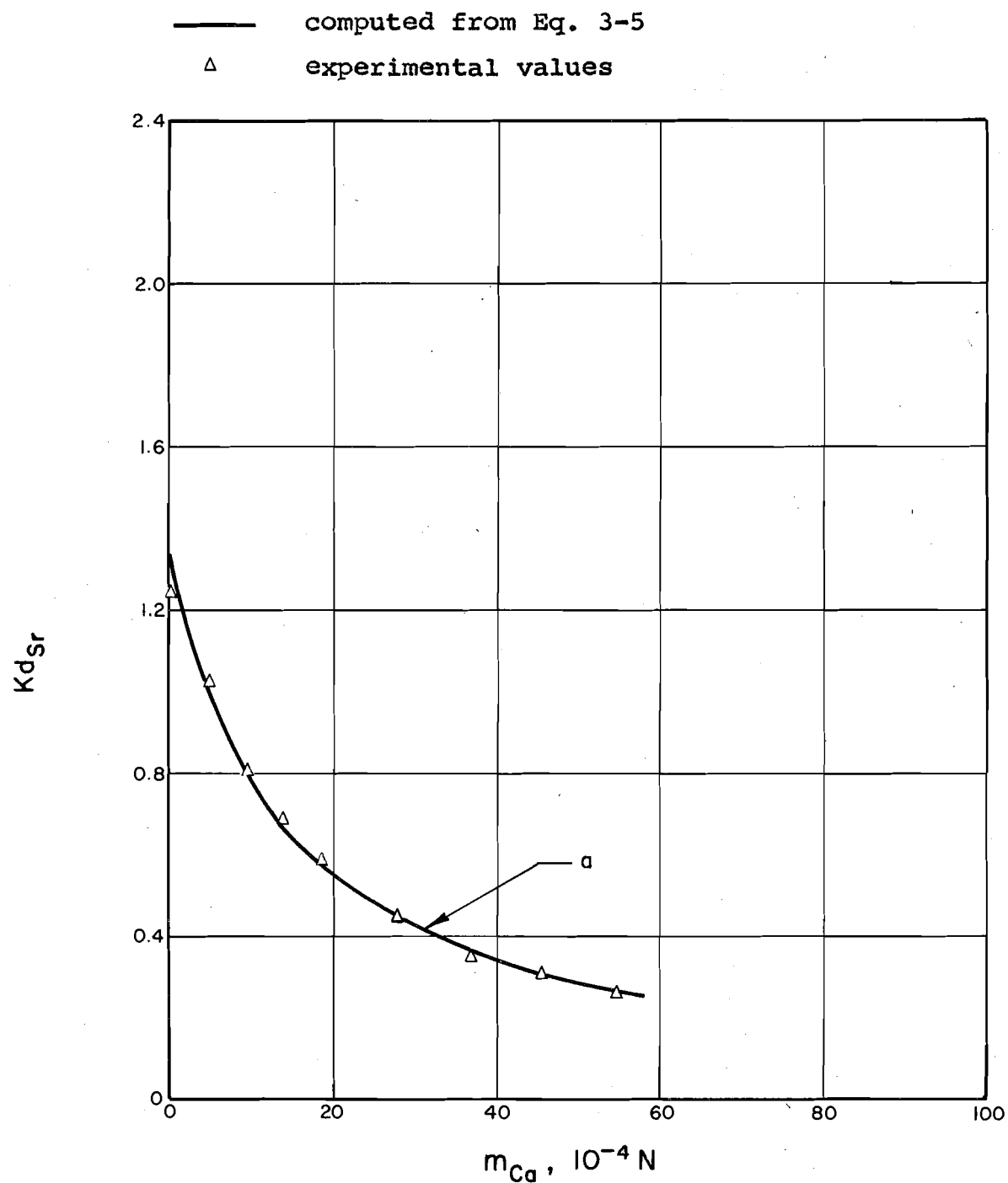


FIG. 16 ION EXCHANGE EQUILIBRIUM OF MONTMORILLONITE WITH FOUR COMPETING COUNTER IONS.

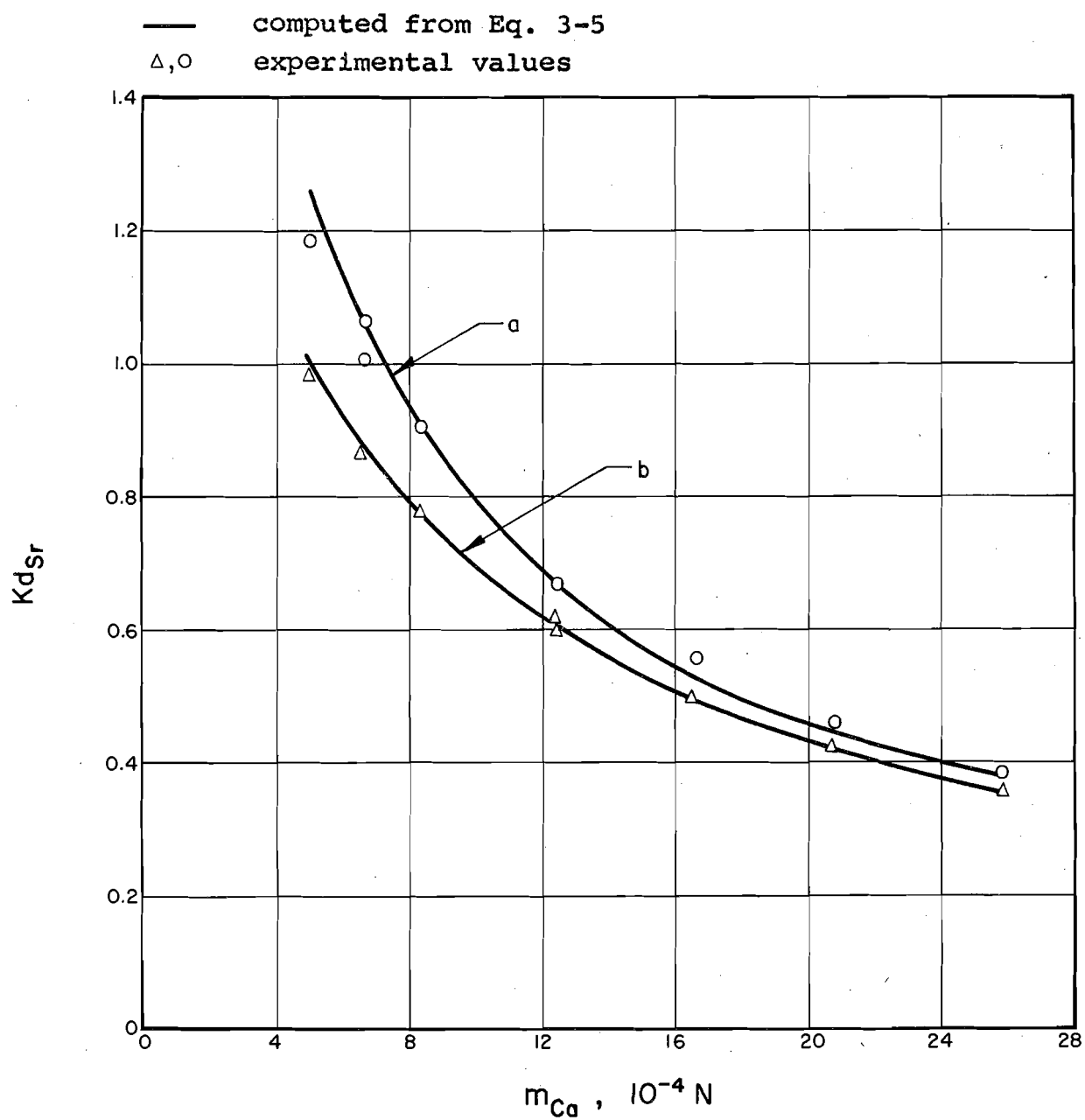


FIG. 17 ION EXCHANGE EQUILIBRIUM OF ILLITE WITH THREE COMPETING COUNTER IONS.

TABLE 10
EXPERIMENTAL CONDITIONS FOR EXCHANGE EQUILIBRIA IN MULTICOMPONENT SYSTEM

	Clay concentration, N	Counter ion concentration, N			
		Na ⁺	Mg ⁺⁺	Sr ⁺⁺	Ca ⁺⁺
Fig. 15, a	Ca-mont.= 1.42×10^{-3}	9.09×10^{-3}	0	1.812×10^{-4}	$0.3.0 \times 10^{-3}$
b	Ca-mont.= 1.42×10^{-3}	0	9.09×10^{-4}	1.812×10^{-4}	$0.3.0 \times 10^{-3}$
Fig. 16	Ca-mont.= 1.795×10^{-3}	1.82×10^{-3}	$4.5-46 \times 10^{-4}$	9.09×10^{-6}	0.10^{-2}
Fig. 17, a	Ca-illite= 9.8×10^{-4}	8.333×10^{-3}	0	8.33×10^{-5}	$0.3.0 \times 10^{-3}$
b	Ca-illite= 9.8×10^{-4}	0	5×10^{-4}	1.666×10^{-5}	$0.3.0 \times 10^{-3}$

5. ION-EXCHANGE EQUILIBRIUM IN PRESENCE OF ORGANICS;

RESULTS AND DISCUSSION

5.1. Effects of Sequestering Agents on Ion-Exchange Reactions of Clay Minerals

Interactions of water-soluble, chelate-forming organic compounds with metal ions and their effects on the ion-exchange reactions of these metal ions have been briefly discussed in Section 2.6.1. An exact quantitative formulation of the ion-exchange equilibria in the presence of sequestering agents is a complex problem. A universally applicable solution does not exist, and if it is possible to produce one, it will be an affair of unmanageable complexity. Even for a qualitative prediction of the behavior of the system, certain assumptions and approximations are necessary.

Equations (2-27), (2-28), and (2-29) are the results of the various assumptions described in Section 2.6.1.

$$\overline{Kd}_A = \frac{\left[K_{OAB} \left(\frac{\bar{m}_B}{\bar{m}_B} \right)^a \right]^{1/b}}{(1 + m_Y \times K_{AY})} \quad (2-27)$$

$$\overline{Kd}_B = \frac{\left[K_{OBA} \left(\frac{\bar{m}_A}{\bar{m}_A} \right)^b \right]^{1/a}}{(1 + m_Y \times K_{BY})} \quad (2-28)$$

$$K_{OAB} = K_{OAB} \frac{(1 + m_Y K_{BY})^a}{(1 + m_Y K_{AY})^b} \quad (2-29)$$

Equations (2-27), (2-28), and (2-29) show the dependency of the counter ion distribution on the sequestering agent concentration (m_Y). Equations (2-27) and (2-28) indicate that the formation of stable sequestered compound prevents the cation from adsorbing on the exchanger, that is the value of \overline{Kd} becomes small. When both cations A^{a+} and B^{b+} form sequestered compounds with Y, the effective equilibrium constant \overline{Ko}_{AB} depends on the ligand concentration and the stability constants of both sequestered compounds. If cation B^{b+} forms a more stable sequestered compound ($K_{BY} > K_{AY}$), then the effective equilibrium constant \overline{Ko}_{AB} is greater than Ko_{AB} , and hence cation A^{a+} is more favorably adsorbed on the exchanger phase when the ligand Y is present. It should be well understood that these equations only describe the system with the conditions imposed by the assumptions that (1) the sequestering agent ($H_n Y$) is in one ionic form (Y^{n-}), (2) the sequestering agents form only one type of chelated compound with A^{a+} and B^{b+} and (3) neither the sequestering agents nor the sequestered metal ions interact with the ion exchanger.

The effects of sequestering agents (citrate, tartrate, and EDTA) on the ion-exchange reactions of soil minerals were investigated by batch equilibrium-type experiments. All the reactions were carried out in 6-ounce Armstrong prescription bottles containing 50 ml of the total solution. The effects of the sequestering agents were examined in terms of changes in equilibrium distributions of the counter ion pairs ($Sr^{++}-Na^+$, $Sr^{++}-Ca^{++}$, $Sr^{++}-Mg^{++}$, and $Sr^{++}-Zn^{++}$) in the presence of these agents. In all the experiments in this section, the concentrations of the inorganic counter ion pairs were kept constant, while the sequestering agents were varied from zero to about twice the concentration of the total

cations. The results of the experiments are summarized in Fig. 18 through Fig. 24.

In Fig. 18 and Fig. 21 (curves a and c), the effects of citrate on the ion-exchange reactions of the various counter ion pairs ($\text{Sr}^{++}\text{-Na}^+$, $\text{Sr}^{++}\text{-Ca}^{++}$, and $\text{Sr}^{++}\text{-Zn}^{++}$) are shown. The experimental conditions are summarized in Table 11. Theoretically, Equation (2-27) should satisfy the experimental data if all assumptions were valid. Rewriting Equation (2-27) in terms of m_{Sr} , m_{Na} , and the experimental conditions, the following equations are obtained,

$$\overline{Kd}_{\text{Sr}} = \frac{K_{\text{O SrNa}} \left(\frac{\overline{m}_{\text{Na}}}{m_{\text{Na}}} \right)^2}{1 + m_{\text{Cit}} K_{\text{SrCit}}} \quad (5-1a)$$

$$K_{\text{SrCit}} = \frac{(m_{\text{SrCit}})}{(m_{\text{Sr}})(m_{\text{Cit}})} \quad (5-1b)$$

$$m_{\text{Sr}}^{\text{O}} = \overline{m}_{\text{Sr}} + m_{\text{Sr}} + m_{\text{SrCit}} \quad (5-1c)$$

$$m_{\text{Cit}}^{\text{t}} = m_{\text{Cit}} + m_{\text{SrCit}} \quad (5-1d)$$

with $K_{\text{O SrNa}} = 1.19 \times 10^3$, $K_{\text{SrCit}} = 0.333 \times 10^{2.7}$,

where all the concentrations are in normal concentrations, and m_{Sr}^{O} and $m_{\text{Cit}}^{\text{t}}$ represent the total amounts of Sr^{++} and citrate added to the system.

The value of the equilibrium constant ($K_{\text{O SrNa}} = 1.19 \times 10^3$) is the average value determined in Section 4.4. The stability constant ($K_{\text{SrCit}} = 0.333 \times 10^{2.7}$) of strontium citrate⁽³⁵⁾ is corrected to be used

	Na^+	Sr^{++}	Clay Minerals, N
a	6×10^{-3}	5×10^{-5}	Na-Mont. = 8.3×10^{-4}
b	2×10^{-3}	1×10^{-4}	Sr-Mont. = 7.8×10^{-4}

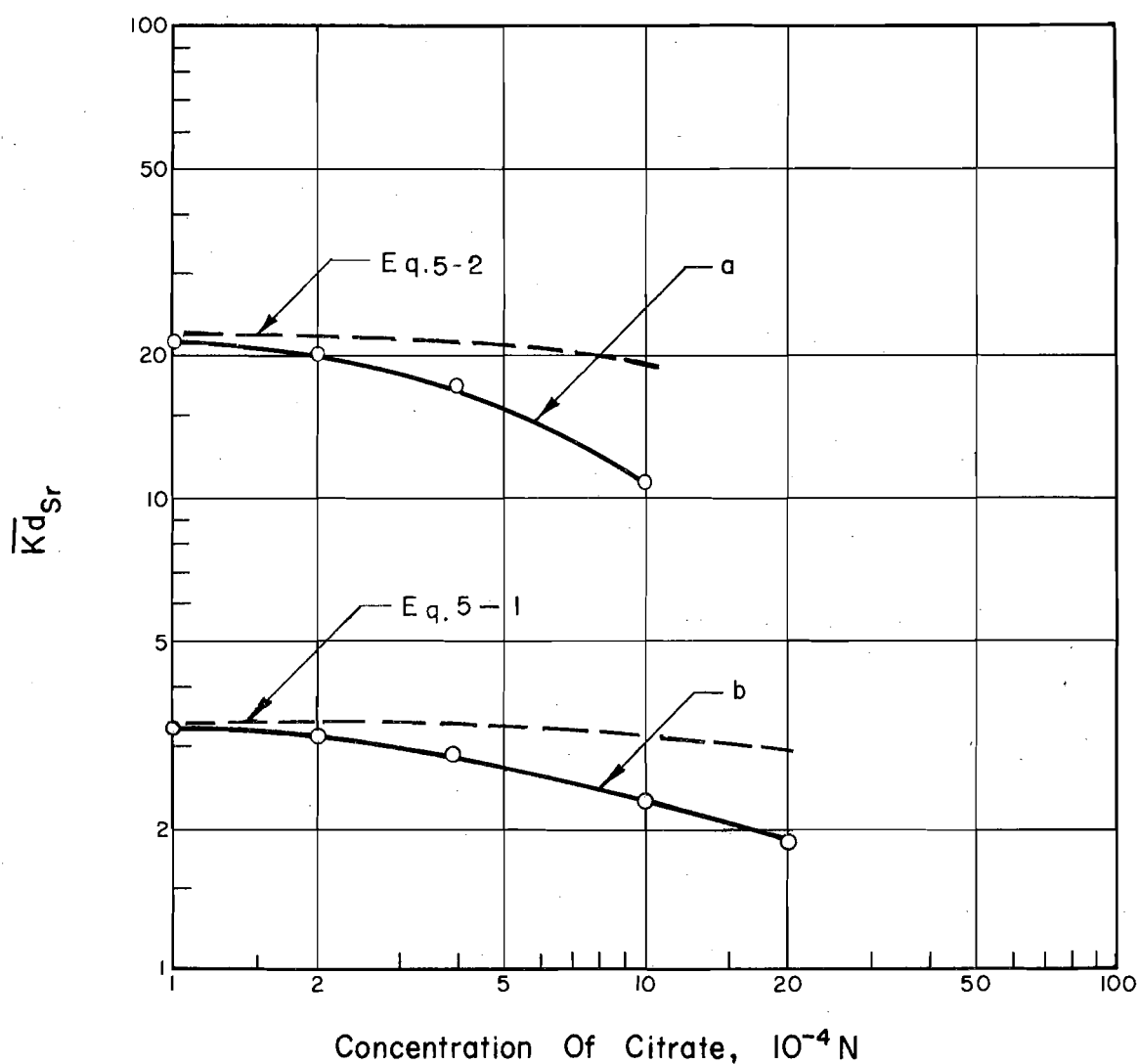


FIG. 18 EFFECTS OF CITRATE ON DISTRIBUTION OF Sr^{++} IN EQUILIBRIUM WITH CLAY AND COMPETING COUNTER IONS.

	Na^+	Sr^{++}	Clay Minerals, N
a,	8×10^{-3}	1×10^{-4}	$\text{Na-Mont.} = 8.3 \times 10^{-4}$
b,	8×10^{-3}	1×10^{-4}	$\text{Sr-Mont.} = 19.0 \times 10^{-4}$

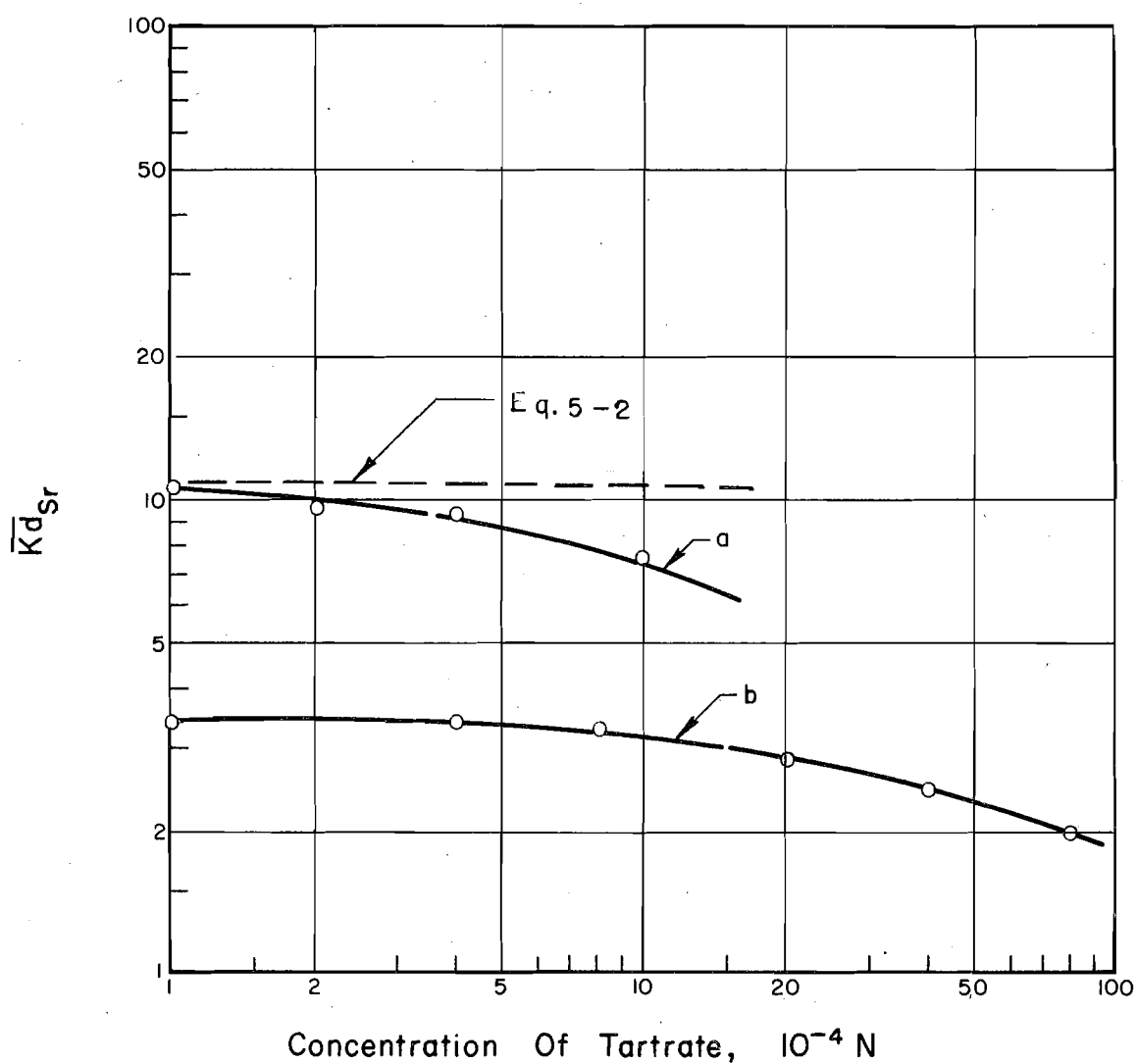


FIG. 19 EFFECTS OF TARTRATE ON DISTRIBUTION OF Sr^{++} IN EQUILIBRIUM WITH CLAY AND COMPETING COUNTER IONS.

	Na ⁺	Sr ⁺⁺	Others	Clay Minerals, N
a	5x10 ⁻³	1x10 ⁻⁴	0	Na-Mont.=7.4x10 ⁻⁴
b	2x10 ⁻³	1x10 ⁻⁴	0	Sr-Mont.=8.2x10 ⁻⁴
c	4x10 ⁻³	1x10 ⁻⁴	Ca ⁺⁺ =10 ⁻³	Na-Mont.=7.4x10 ⁻⁴
d	2x10 ⁻³	8x10 ⁻⁴	Mg ⁺⁺ =10 ⁻³	Na-Mont.=7.4x10 ⁻⁴

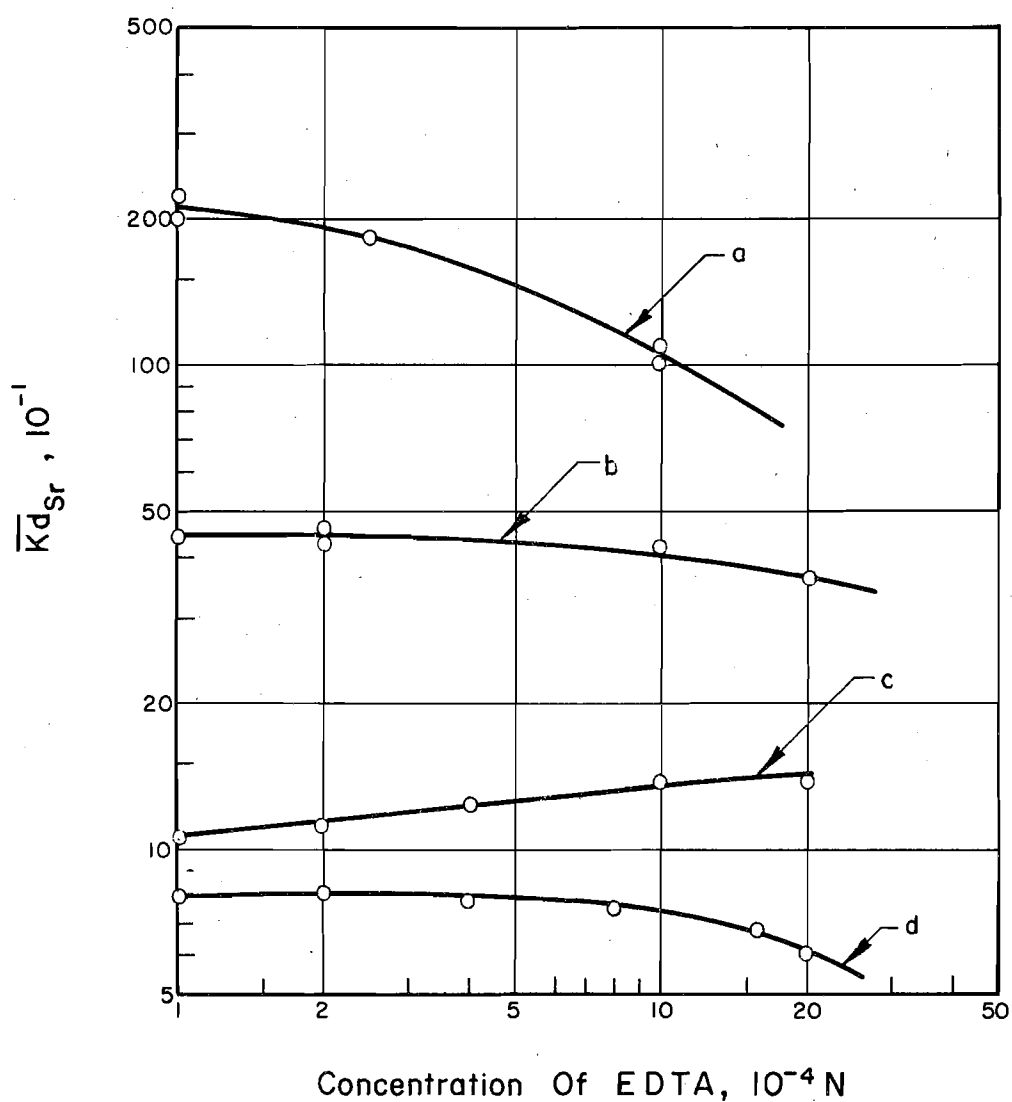


FIG.20 EFFECTS OF EDTA ON DISTRIBUTION OF Sr⁺⁺ IN EQUILIBRIUM WITH CLAY AND COMPETING COUNTER IONS.

	Na^+	Sr^{++}	Others	Clay Minerals, N	Agents
a	4×10^{-3}	2×10^{-4}	$\text{Zn}^{++} = 10^{-3}$	$\text{Sr-Mont.} = 8.2 \times 10^{-4}$	Citrate
b	4×10^{-3}	2×10^{-4}	$\text{Zn}^{++} = 10^{-3}$	$\text{Sr-Mont.} = 8.2 \times 10^{-4}$	EDTA
c	4×10^{-3}	5×10^{-5}	$\text{Ca}^{++} = 10^{-3}$	$\text{Na-Mont.} = 8.3 \times 10^{-4}$	Citrate
d	4×10^{-3}	5×10^{-5}	$\text{Ca}^{++} = 10^{-3}$	$\text{Na-Mont.} = 7.4 \times 10^{-4}$	Tartrate

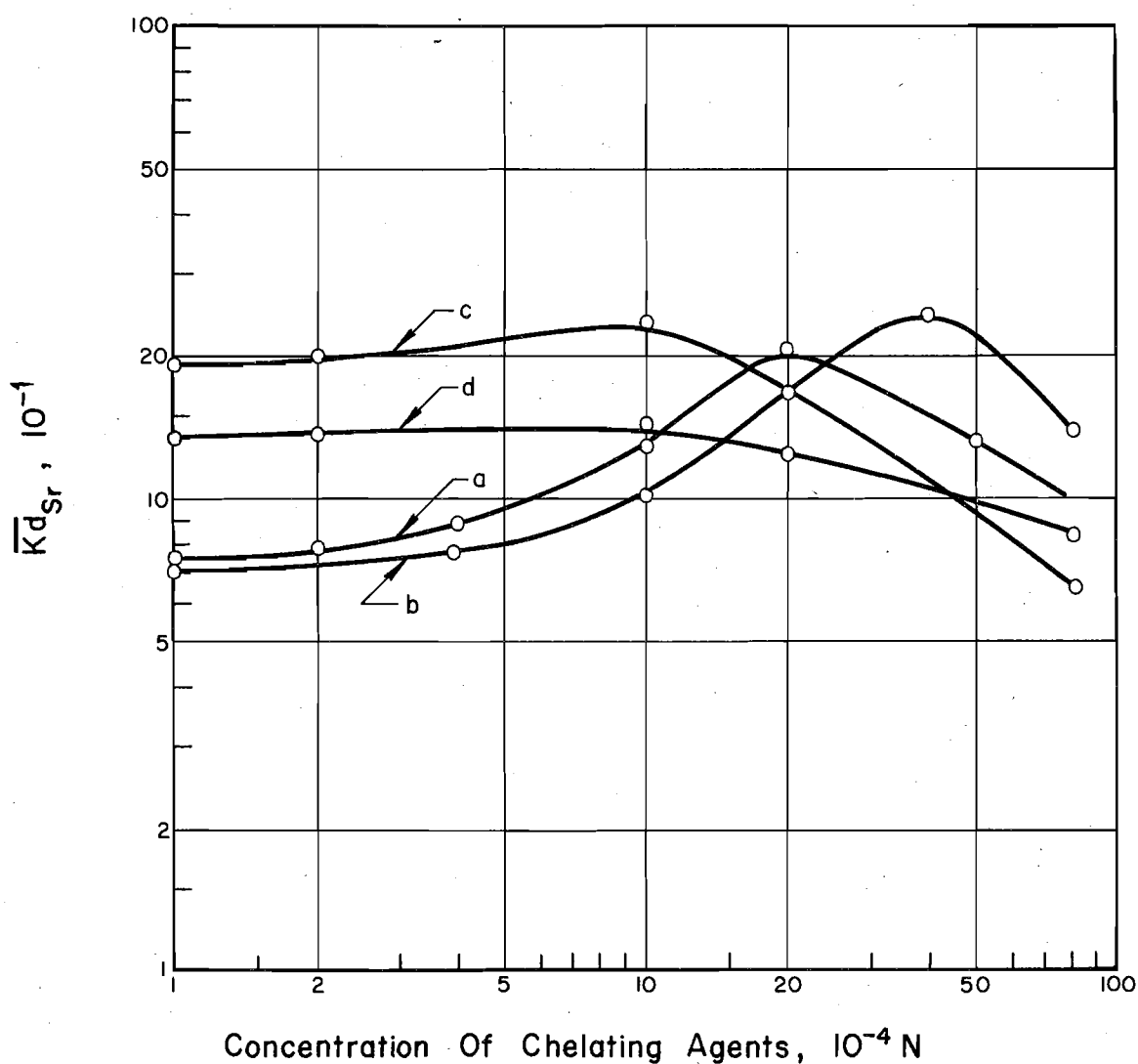


FIG. 21 EFFECTS OF CHELATING AGENTS ON DISTRIBUTION OF Sr^{++} IN EQUILIBRIUM WITH CLAY AND COMPETING COUNTER IONS.

with normal concentrations.

In the case of Fig. 18 (curve a), in which $m_{\text{Sr}}^{\circ} \ll m_{\text{Na}}^{\circ}$, $m_{\text{Sr}}^{\circ} \ll \bar{m}_{\text{Na}}$, and $m_{\text{Sr}}^{\circ} \ll m_{\text{Cit}}^{\circ}$, it can be approximated that $\bar{m}_{\text{Na}} \approx \text{C.E.C.}$, $m_{\text{Na}}^{\circ} \approx m_{\text{Na}}$, and $m_{\text{Cit}}^{\circ} \approx m_{\text{Cit}}^{\text{t}}$. With an additional assumption that all citrate ions are ionized as tertiary citrate (Y^{3-}), Equation (5-1a) becomes,

$$\bar{K}_{\text{d}}^{\text{Sr}} = \frac{K_{\text{SrNa}}^{\circ} \left(\frac{\bar{m}_{\text{Na}}}{m_{\text{Na}}} \right)^2}{1 + m_{\text{Cit}}^{\text{t}} K_{\text{SrCit}}} \quad (5-2)$$

TABLE 11

EXPERIMENTAL CONDITIONS FOR THE STUDY OF EFFECTS OF CITRATE
ON CLAY ION-EXCHANGE REACTIONS

Cations, N			Clay minerals	pH	Figure
Na^{+}	Sr^{++}	others	N		Number
6×10^{-3}	5×10^{-5}	0	Na-Mont. = 8.3×10^{-4}	7.0-7.1	18-a
2×10^{-3}	1×10^{-4}	0	Sr-Mont. = 7.8×10^{-4}	7.1-7.3	18-b
4×10^{-3}	2×10^{-4}	$\text{Zn}^{++} = 10^{-3}$	Sr-Mont. = 8.2×10^{-4}	7.1-7.3	21-a
4×10^{-3}	5×10^{-5}	$\text{Ca}^{++} = 10^{-3}$	Na-Mont. = 8.3×10^{-4}	6.8-7.0	21-c

The effective distribution coefficient $\bar{K}_{\text{d}}^{\text{Sr}}$ computed from Equation (5-2) is shown as a dotted line on the same figure, Fig. 18. When Sr^{++} ions are presented as gross concentration (Fig. 18, curve b), the above approximations are not valid. \bar{m}_{Na} and m_{Cit} can no longer be treated as constant values. The system must satisfy the set of simultaneous equations, Equation (5-1). The solutions of the simultaneous equations are

presented as a dotted line in Fig. 18 (curve b).

In Fig. 21 (curve c), the effects of citrate on the ion-exchange reactions of the counter ion pair $\text{Sr}^{++}\text{-Ca}^{++}$ are shown. Because the citrate added to the system was in the form of sodium citrate, the presence of Na^+ ions in the system was unavoidable. To make the influence of Na^+ ions in the system more or less constant, the concentrations of Na^+ ions in the system were kept at a constant value (4×10^{-3} N) by adding NaCl.

The effects of tartrate on soil ion-exchange reactions were studied in a similar manner as that with citrate. The experimental results are shown in Fig. 19 and Fig. 21 (curve d). The effects of EDTA were studied for the counter ion pairs $\text{Sr}^{++}\text{-Na}^+$, $\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$, and $\text{Sr}^{++}\text{-Zn}^{++}$. The experimental results with EDTA are shown in Fig. 20 and Fig. 21 (curve b). The experimental conditions for the study of the effects of tartrate and EDTA are summarized in Tables 12 and 13.

In general, the experimental results are in good agreement with the qualitative rules for the selectivity of ion exchangers (clay minerals) and the stability of metal chelates. The effects of a sequestering agent on the distribution of Sr^{++} ions in equilibrium with a soil exchange system depend on the nature of the other counter ion present. In the presence of the counter ions that form less stable chelates with the sequestering agent, the Sr^{++} ion concentrations in the solution were increased as sequestering agents were added. These effects were observed in all exchange reactions where Sr^{++} ions were competing with Na^+ ions. The same effects, but less in their intensities, were noticed in the reactions involving the pair, $\text{Sr}^{++}\text{-Mg}^{++}$. On the other hand, when the

TABLE 12
EXPERIMENTAL CONDITIONS FOR THE STUDY OF EFFECTS OF TARTRATE
ON CLAY ION-EXCHANGE REACTIONS

Cations, N			Clay minerals	pH	Figure
Na ⁺	Sr ⁺⁺	others	N		Number
8×10^{-3}	1×10^{-4}	0	Na-Mont. = 8.3×10^{-4}	6.2-6.8	19-a
8×10^{-3}	1×10^{-4}	0	Sr-Mont. = 19.0×10^{-4}	6.2-6.5	19-b
4×10^{-3}	5×10^{-5}	Ca ⁺⁺ = 10^{-3}	Na-Mont. = 7.4×10^{-4}	6.0-6.5	21-d

TABLE 13
EXPERIMENTAL CONDITIONS FOR THE STUDY OF EFFECTS OF EDTA
ON CLAY ION-EXCHANGE REACTIONS

Cations, N			Clay minerals	pH	Figure
Na ⁺	Sr ⁺⁺	others	N		Number
5×10^{-3}	1×10^{-4}	0	Na-Mont. = 7.4×10^{-4}	7.2-7.4	20-a
2×10^{-3}	1×10^{-4}	0	Sr-Mont. = 8.2×10^{-4}	6.0-7.0	20-b
4×10^{-3}	1×10^{-4}	Ca ⁺⁺ = 10^{-3}	Na-Mont. = 7.4×10^{-4}	6.0-6.4	20-c
2×10^{-3}	8×10^{-4}	Mg ⁺⁺ = 10^{-3}	Na-Mont. = 7.4×10^{-4}	5.8-6.5	20-d
4×10^{-3}	2×10^{-4}	Zn ⁺⁺ = 10^{-3}	Sr-Mont. = 8.2×10^{-4}	5.5-6.5	21-b

counter ions (Ca^{++} , Zn^{++}) that form more stable chelated compounds were present, the Sr^{++} ion concentrations in the solution phase were decreased as the agents were added.

As shown in Fig. 18, the experimental results indicate that the effects of citrate are even greater than theoretically predicted. It is not clear what factors cause the experimental values to show the greater effects than theoretically predicted. Possible reasons may be found in the assumptions made to evaluate the theoretical predictions.

The assumption that all citrate ions are ionized as tertiary citrate (Y^{3-}) seems to be accurate. The percentage of an ionized acid may be computed from the expression⁽⁴¹⁾,

$$\% \text{ Ionized} = \frac{100}{1 + \text{antilog}(\text{pKa} - \text{pH})} \quad (5-3)$$

For the value of $\text{pKa} = 5.49$ (Table 2) and $\text{pH} 7$ (experimental condition), the percentage of tertiary citrate (Y^{3-}) is 98%, which indicates that at $\text{pH} 7$ the ionization of citrate ion is practically complete.

It has been shown⁽³⁵⁾ that citrate ions are involved in three different chelate formations with Ca^{++} ions (CaY^- , CaHY , CaH_2Y^+); however, their stability constants differ by factors of more than 10, and hence the assumption that citrate ions form only one chelated compound, that is, the most stable compound, seems quite reasonable. At present, the stability constant of Sr -citrate is reported for only one compound (SrY^-). There are some discrepancies in the reported values of metal chelate stability constants. For instance, in the case of Ca -citrate (CaY^-), values^(35, 40) of $K = 10^{3.2}$ to $K = 10^{4.9}$ have been reported. Using the

experimental data (Fig. 21, curve a) and Equation (5-2), the stability constants of Sr-citrate are calculated for citrate concentrations of 4×10^{-4} and 10^{-3} N. The values are $10^{3.4}$ and $10^{3.5}$. There is no clear evidence that using a value of $K_{\text{SrCit}} = 10^{2.7}$ in the evaluation of the theoretical prediction was wrong; however, it is of interest to note that the prediction is in good agreement if a K_{SrCit} value of $10^{3.4}$ is used.

To determine if sequestering agents or the sequestered compounds interacted with clay minerals, experiments were performed in which citrate adsorption was determined with C^{14} -labelled tracers. The experimental results are summarized in Figs. 22, 23, and 24. It is shown that all the sequestering agents were adsorbed on the clay minerals; however, in the case of EDTA, the adsorption was much lower than with either citrate or tartrate. The adsorption of the sequestering agents on clay minerals was found to depend on the concentration of electrolyte in the solution and exchanger phases. It is not known what physical mechanisms were involved in this adsorption. Increase in the adsorption of the organic anion (Fig. 24) at higher electrolyte concentrations (NaCl) suggests that anion exchange was not involved. The adsorption of sequestering agents on clay minerals further complicates the quantitative analysis of the exchange reactions in the presence of these agents.

The effects of citrate are in general greater than those of tartrate. This is expected, since with most metal ions, citrate forms more stable sequestered compounds than does tartrate. The chelate formation of EDTA is pH dependent. For example, at pH 7, EDTA (H_4Y) ionizes into three different ions Y^{4-} (0.055%), HY^{3-} (87.5%), and H_2Y^{2-} (12.5%). Even though only 0.055% are in the form of Y^{4-} , because of its high

	Na ⁺	Sr ⁺⁺	Clay Minerals, N
a,	2×10^{-3}	1×10^{-4}	Sr-Mont.= 7.8×10^{-4}
b,	2×10^{-3}	1×10^{-4}	Sr-Illite= 2.0×10^{-4}
c,	6×10^{-3}	5×10^{-5}	Na-Mont.= 8.3×10^{-4}
d,	0	0	Sr-Mont.= 7.8×10^{-4}
e,	0	0	Na-Mont.= 8.3×10^{-4}

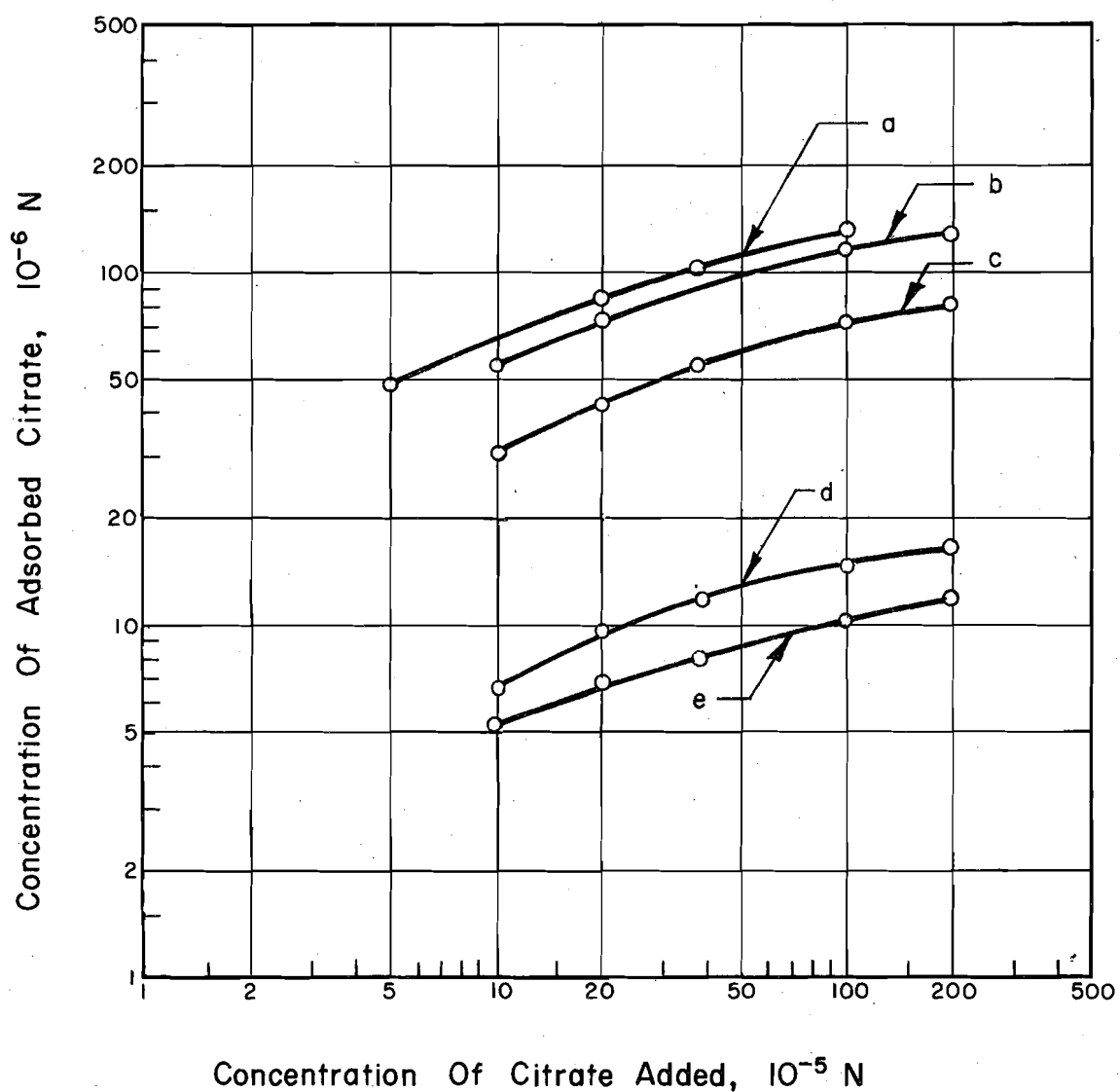


FIG. 22 ADSORPTION OF CITRATE ON CLAY MINERALS.

	Na^+	Sr^{++}	Clay Minerals, N	Agents
a,	8×10^{-3}	1×10^{-4}	$\text{Sr-Mont.} = 7.8 \times 10^{-4}$	Tartrate
b,	8×10^{-3}	5×10^{-5}	$\text{Na-Mont.} = 8.3 \times 10^{-4}$	Tartrate
c,	2×10^{-3}	1×10^{-4}	$\text{Sr-Mont.} = 7.4 \times 10^{-4}$	EDTA

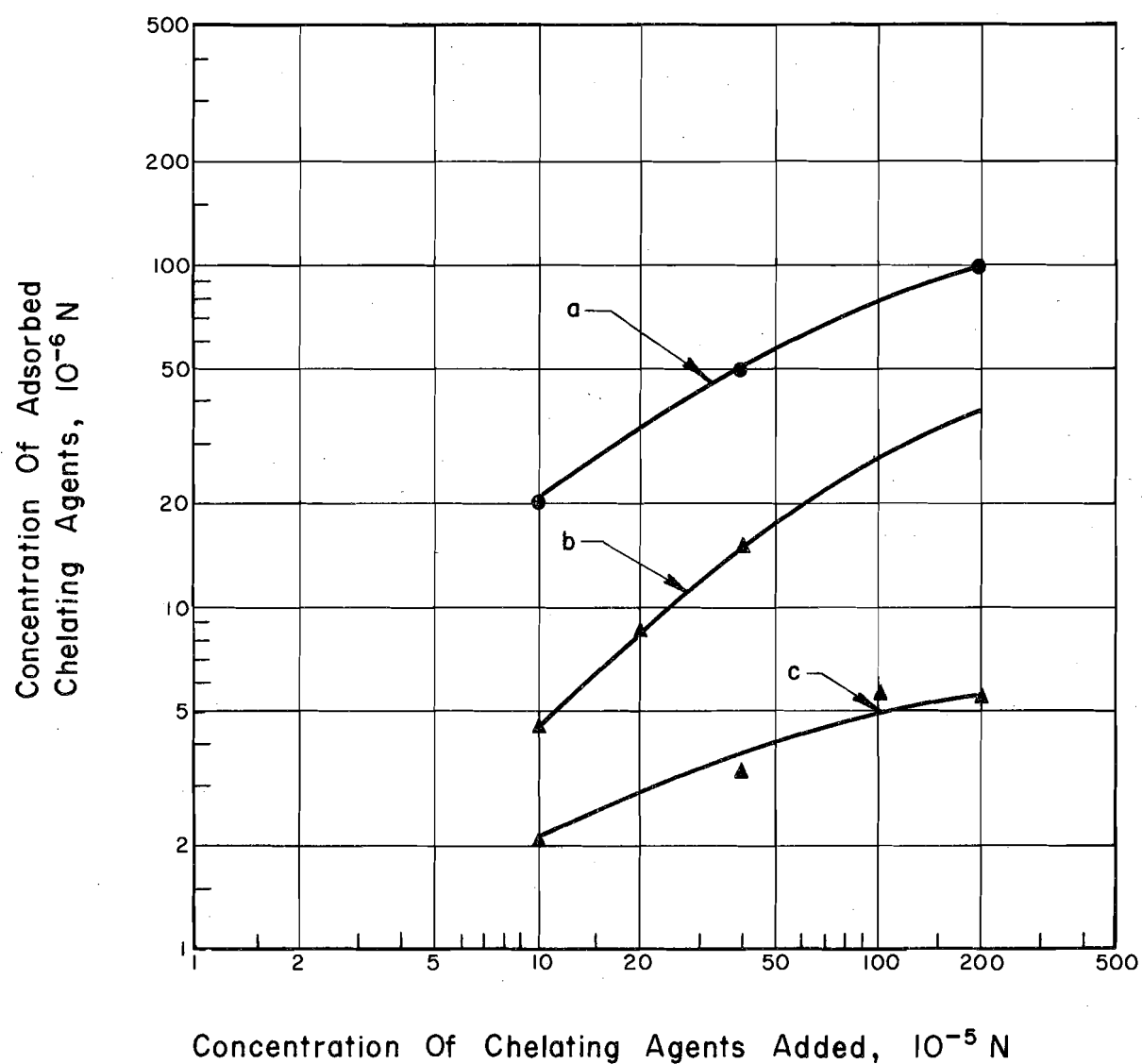


FIG. 23 ADSORPTION OF CHELATING AGENTS ON CLAY MINERALS.

	Citrate, N	Clay Minerals, N
a,	1×10^{-4}	Na-Mont.= 8.3×10^{-4}
b,	1×10^{-5}	Na-Mont.= 8.3×10^{-4}
c,	1×10^{-5}	Na-Illite= 2.0×10^{-4}

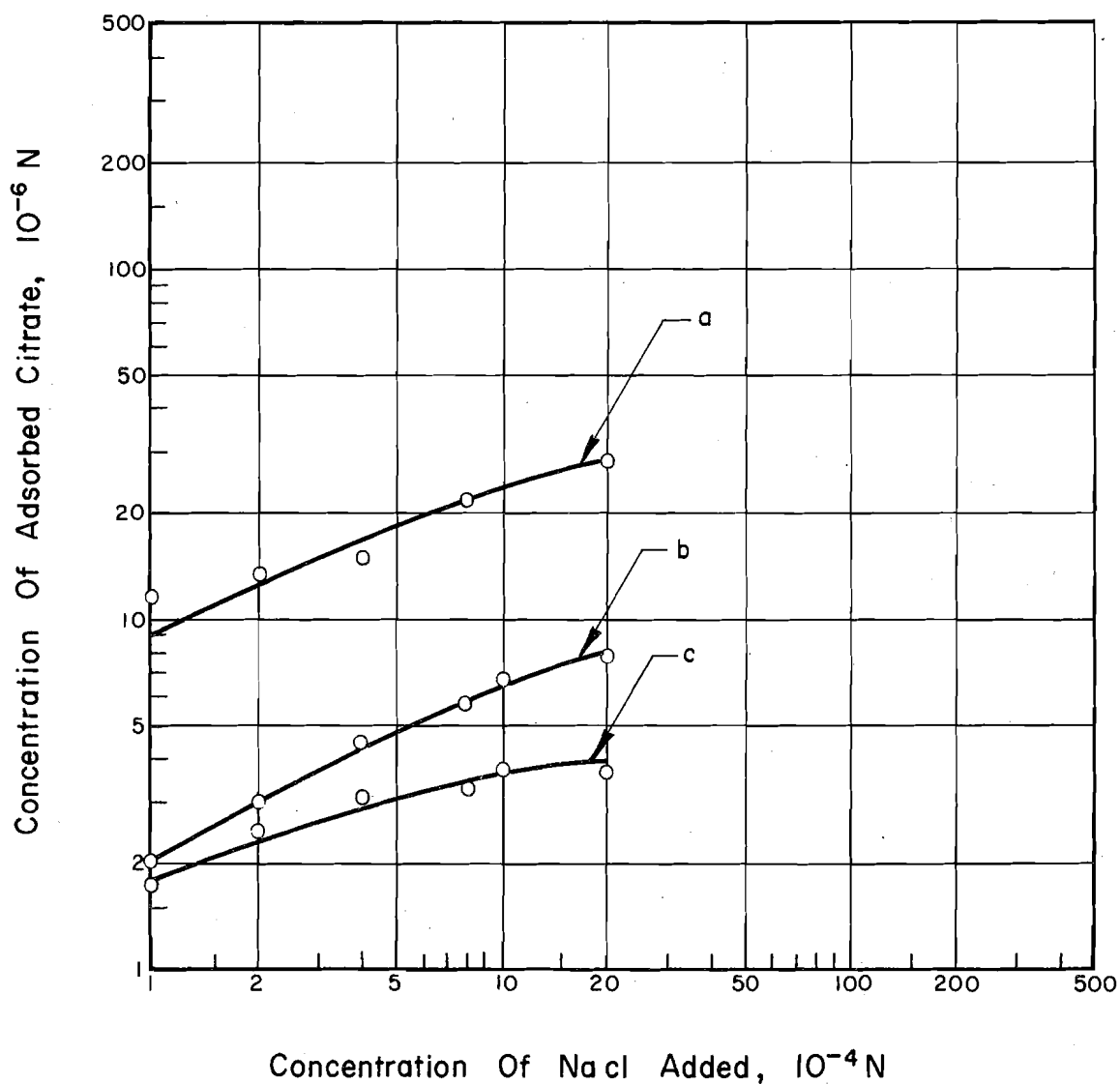


FIG. 24 ADSORPTION OF CITRATE ON CLAY MINERALS AS A FUNCTION OF NaCl ADDED.

stability, most of Sr-EDTA is in the form of SrY^{2-} . At a higher pH, the effect of EDTA will be much greater than that of citrate or tartrate.

Summarizing the results of the study of the effects of sequestering agents, it can be concluded that the results are in good agreement with the general rules for the selectivity of soil exchange media and the stability of metal chelates.

It can be shown that ⁽²⁶⁾ the velocity (R_{Sr}) of Sr^{++} ion relative to the velocity of water (R_w) containing Sr^{++} in a soil exchange medium is

$$\frac{R_{\text{Sr}}}{R_w} = \frac{1}{1 + \overline{Kd}_{\text{Sr}}}, \quad (5-4)$$

which shows that the rate of migration of Sr^{++} depends on the effective distribution coefficient, $\overline{Kd}_{\text{Sr}}$. Assuming the concentration of a sequestering agent in natural water in contact with soil exchange media to be about 10 mg/l as citric acid (5.2×10^{-5} N), which may be considered as a high organic content in natural water, it can be shown from Equation (5-1) that the change in the effective distribution of Sr^{++} is less than one percent. It is not probable that in a natural environment, the concentration of a sequestering agent is so high as to give significant effects on the movement of radionuclides disposed into the environment. The presence of a noticeable concentration of sequestering agents, which may be found in certain nuclear wastes, may even be beneficial in terms of contaminating the water system; for in the presence of a sequestering agent the hazardous radionuclides such as Sr^{90} and Cs^{137} will be more favorably adsorbed on soil if the system contains gross concentrations of

competing counter ions such as Ca^{++} and Al^{3+} , because they are more strongly sequestered than Sr^{++} or Cs^+ .

5.2. Adsorption of Organic Compounds and Effects on the Clay Ion-Exchange Properties

Interactions of soil-sorptive organic compounds with clay minerals were briefly discussed in Section 2.6.2. There has been considerable work done in the field of organic adsorption on clay minerals. Grim⁽¹³⁾ has presented a comprehensive survey of this subject. The effects of organic adsorption on the ion-exchange properties of soil minerals is a problem deserving some attention. The investigations in this area will not only aid the understanding of organic-clay reactions, but will also furnish information regarding the fundamental mechanisms involved in soil ion-exchange reactions.

In this section, studies of organic-clay interactions were carried out to learn the effects of organic adsorption on the ion-exchange properties of soil minerals. In general, the effects of the organic-clay interactions were examined in terms of changes in the soil ion-exchange parameters such as the exchange capacities and the selectivities of the soil minerals.

5.2.1. Adsorption of Methylene Blue and Its Effect on the Clay Ion-Exchange Properties

Methylene blue has a unique property in the sense that it can be irreversibly adsorbed on clay surfaces to block out any desired portion of the clay exchange sites without the presence of residual

methylen blue in the solution phase. This allows study of the effects of its presence only in the exchanger phase. In addition, its large size makes possible the study of the effects of methylen blue on covering-up of the exchange sites. Comparing the effective area of the methylen blue molecule with that of coedine⁽²⁷⁾ which has about the same configuration as the methylen blue molecule, the effective area of the methylen blue ion may be approximated to be about 150 \AA^2 . The interactions of methylen blue ions (M.B.^+) with clay minerals were carried out to study: (1) the selectivity of clay minerals for M.B.^+ , (2) the covering-up effects of M.B.^+ , and (3) the effects of adsorbed M.B.^+ on the selective properties of the available exchange sites for various counter ions.

The attempt to determine the relative selectivity of clay minerals for M.B.^+ ion with respect to Sr^{++} was unsuccessful, because the selectivity for M.B.^+ was so strong that the exchange adsorption of M.B.^+ was practically irreversible. Regardless of the concentration of the counter ion, Sr^{++} (up to 10^{-2} N), the adsorption of M.B.^+ continued until all the exchange sites were occupied with M.B.^+ ions.

The cover-up effects of the adsorbed M.B.^+ ions were investigated by examining the adsorption of Sr^{++} ions ($2 \times 10^{-3} \text{ N}$) on Na-montmorillonite whose exchange sites were previously covered (0-100%) with M.B.^+ ions. Similar experiments, with the exception that the M.B.^+ ions were added after the Sr^{++} ions were equilibrated with Na-montmorillonite, were also carried out. The difference between the two experiments was that in the first experiment, the cover-up effects would be shown as less Sr^{++} adsorption, whereas in the second experiment the cover-up effects would be shown as trapping some of adsorbed Sr^{++} ions. Similar

experiments were also performed with Na-illite. As shown in Figs. 25 and 26, for both montmorillonite and illite, $M.B.^+$ ions were able to smother the exchange sites. The degree of the cover-up effects depended on the amounts of the adsorbed $M.B.^+$ ions. The cover-up effects increased as the adsorbed amounts of $M.B.^+$ increased. Comparing the results for montmorillonite and illite, it is evident that the degree of the cover-up effects were about the same for both clay minerals, even though the locations of the exchange sites in the two minerals may have been quite different, illite minerals having most of the exchange sites at the edges of the basal planes, whereas in montmorillonite most of the exchange sites are on the basal planes.

The effects of the adsorbed $M.B.^+$ on the selective properties of the available exchange sites were investigated for the counter ion pairs $Sr^{++}-Ca^{++}$ and $Sr^{++}-Na^+$. The ion-exchange reactions between Sr^{++} and Ca^{++} were carried out with Ca-clay minerals whose exchange sites were partially covered with $M.B.^+$ ions (0, 15, 30, and 50%). Similar experiments were also conducted for $Sr^{++}-Na^+$ with Na-clay minerals. The experimental results are summarized in Figs. 27 through 30. The effects of $M.B.^+$ on the ion-exchange reactions between Sr^{++} and Ca^{++} with montmorillonite and illite are shown in Figs. 27 and 28, in which the ratio of the counter ion concentrations in the exchanger phase ($\frac{\bar{m}_{Sr}}{\bar{m}_{Ca}}$) is plotted as a function of the ratio in the solution phase. The ratio of the values of the ordinate to the abscissa is a mass-action equilibrium constant without the activity corrections. The effects of $M.B.^+$ on the exchange reactions between Sr^{++} and Na^+ with montmorillonite and illite are shown in Figs. 29 and 30. In Fig. 29, the mass-action equilibrium constants

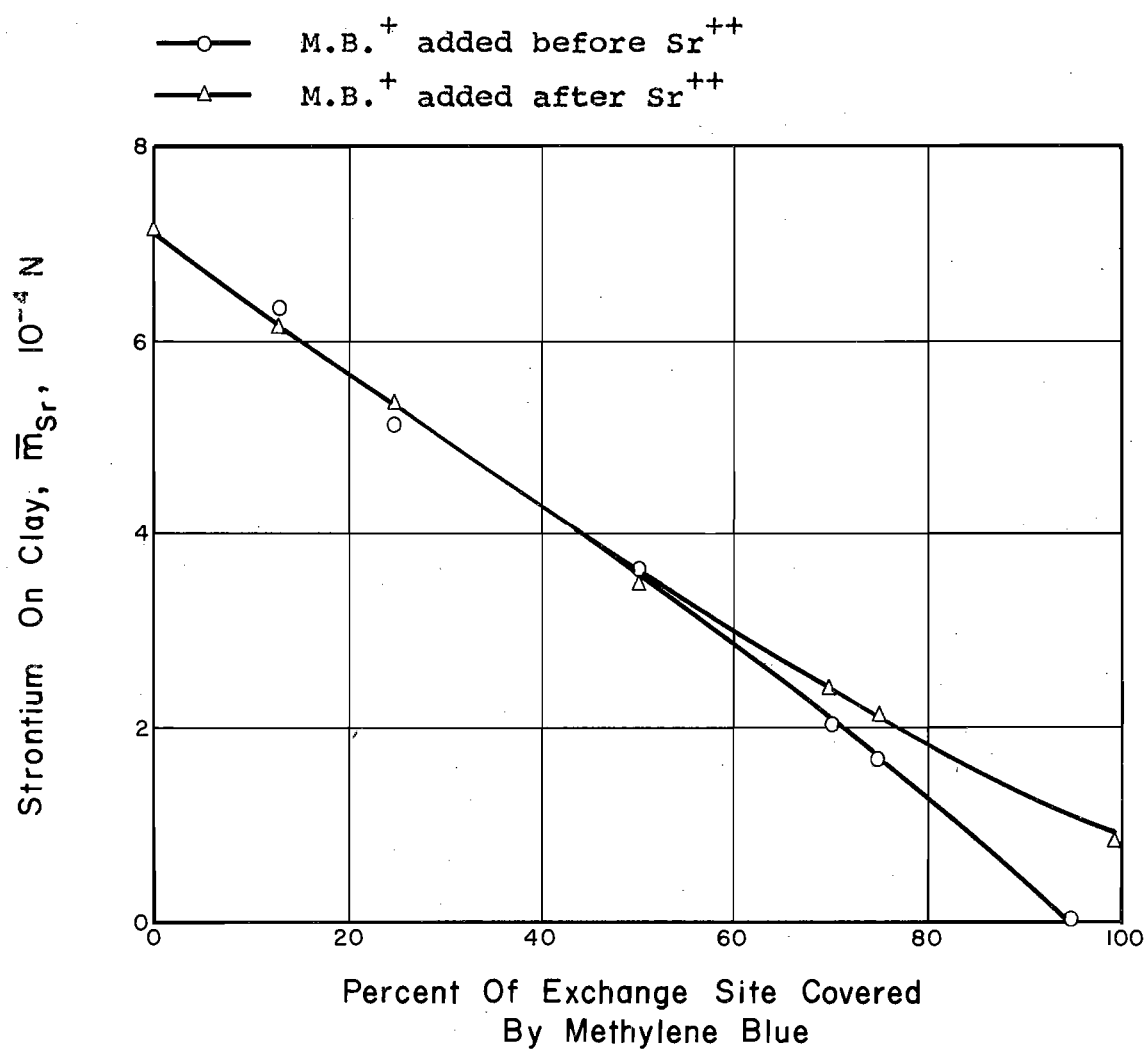


FIG. 25 ADSORPTION OF METHYLENE BLUE ON MONTMORILLONITE AND EFFECTS ON EXCHANGEABLE CATIONS, Sr⁺⁺.

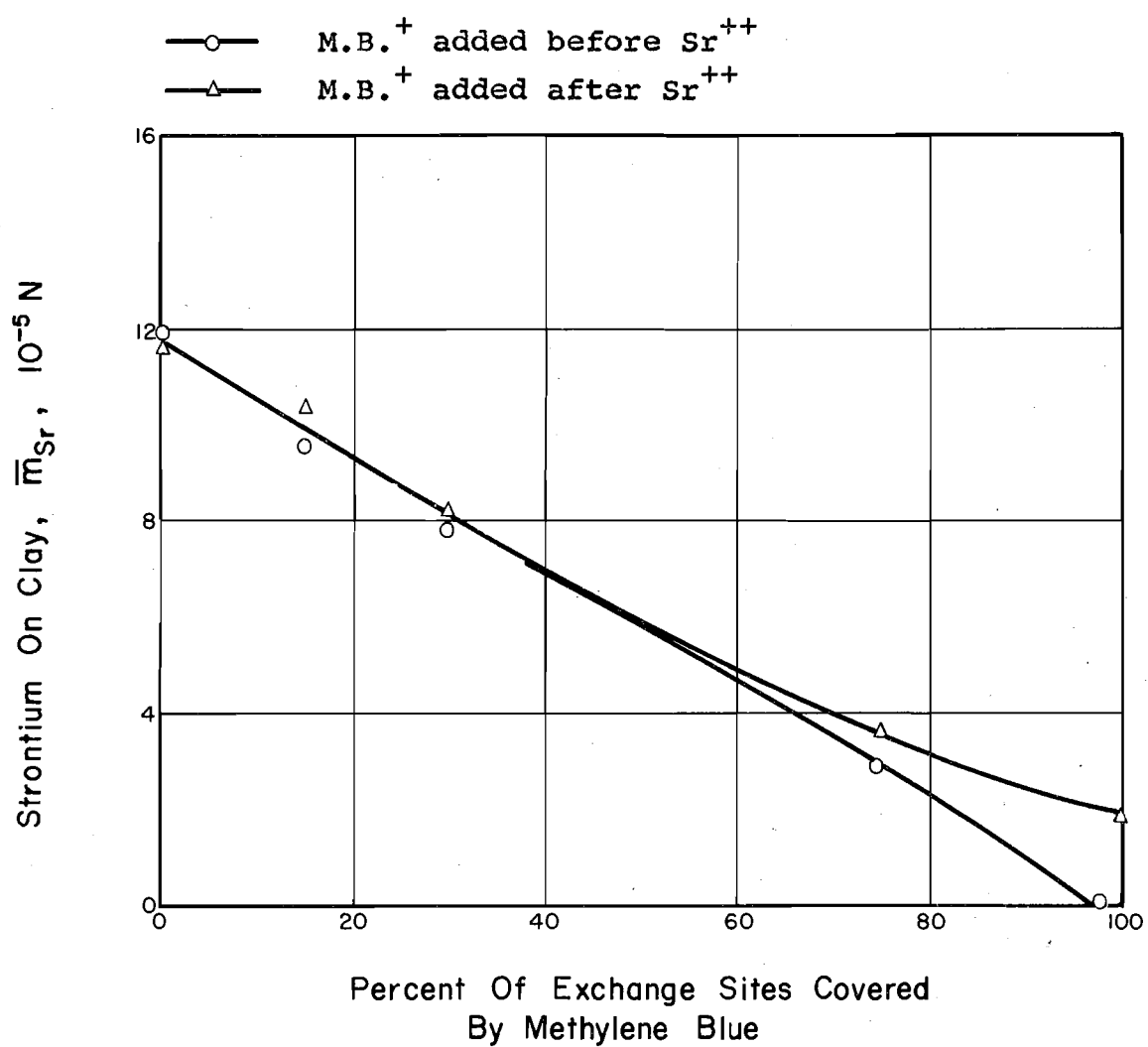


FIG. 26 ADSORPTION OF METHYLENE BLUE ON ILLITE AND EFFECTS ON EXCHANGEABLE CATION, Sr⁺⁺.

$$m_{\text{Sr}}^{\text{O}} = 1 \times 10^{-4} - 1 \times 10^{-3}; \quad m_{\text{Ca}}^{\text{O}} = 1 \times 10^{-3}; \quad \text{Ca-Mont.} = 8.7 \times 10^{-4}$$

	a	b	c	d
% covered by M.B. +	0	15	30	50

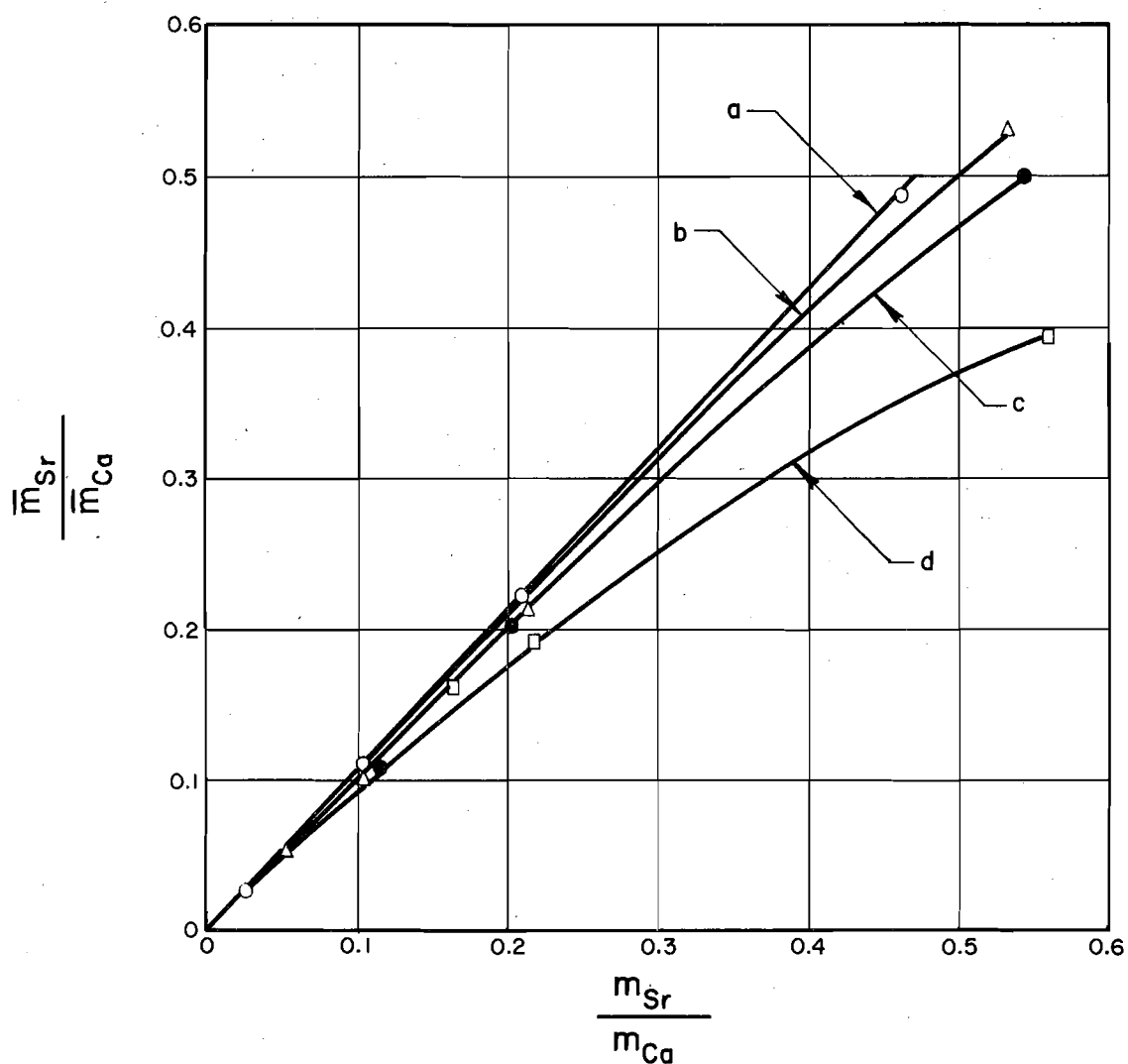


FIG. 27 EFFECT OF METHYLENE BLUE ON EQUILIBRIUM DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Ca^{++} , FOR Ca-MONTMORILLONITE.

$$m_{\text{Sr}}^{\circ} = 5 \times 10^{-5} - 2 \times 10^{-4}; \quad m_{\text{Ca}}^{\circ} = 5 \times 10^{-4}; \quad \text{Ca-Illite} = 4.95 \times 10^{-4} \text{ N}$$

	a	b	c
% covered by M.B. ⁺	0	18	36

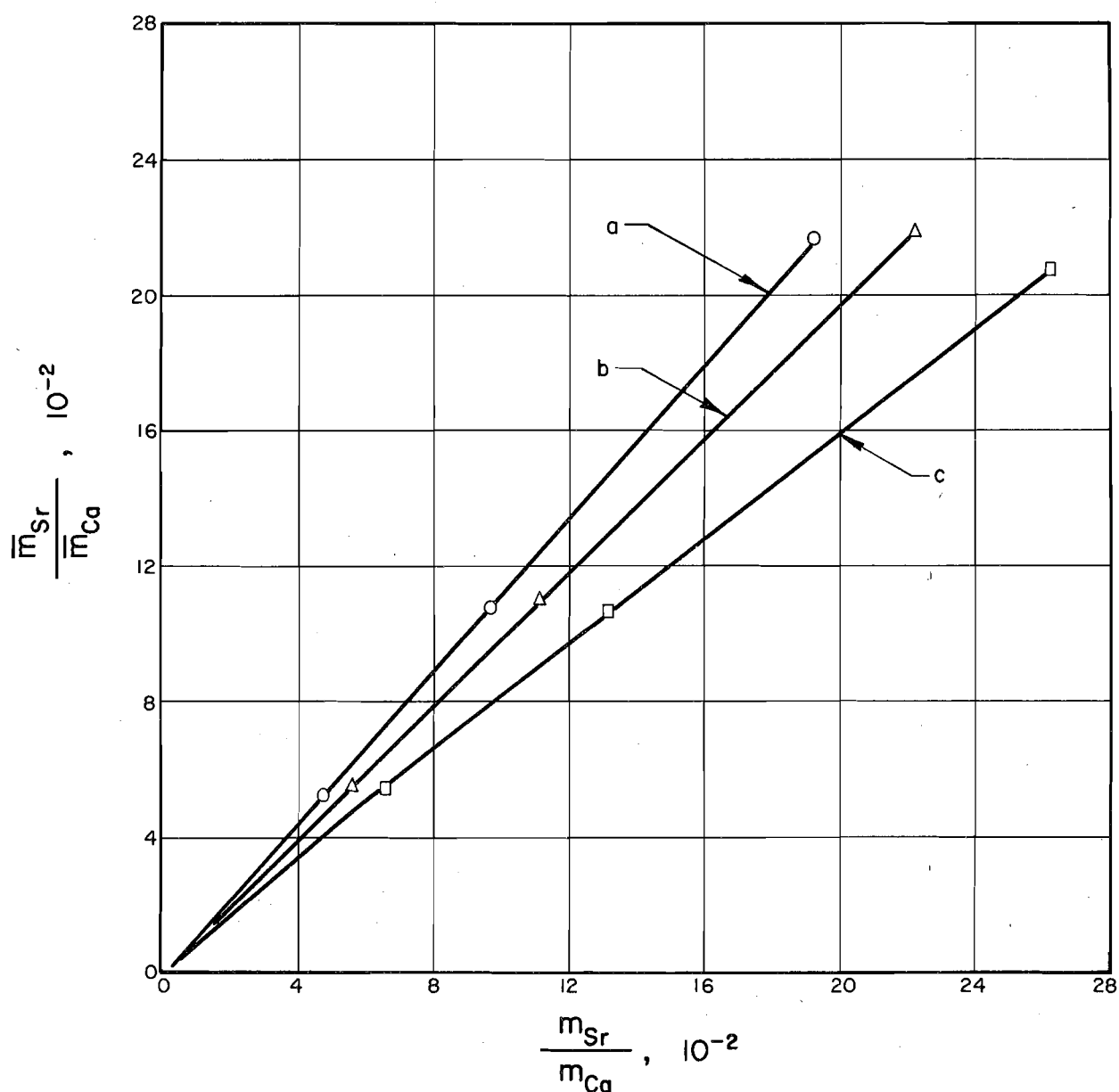


FIG. 28 EFFECT OF METHYLENE BLUE ON EQUILIBRIUM DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Ca^{++} , FOR Ca-ILLITE.

$$m_{\text{Na}}^{\text{O}} = 1 \times 10^{-2}; \quad m_{\text{Sr}}^{\text{O}} = 1 \times 10^{-4}; \quad \text{Na-Mont.} = 8.82 \times 10^{-4}$$

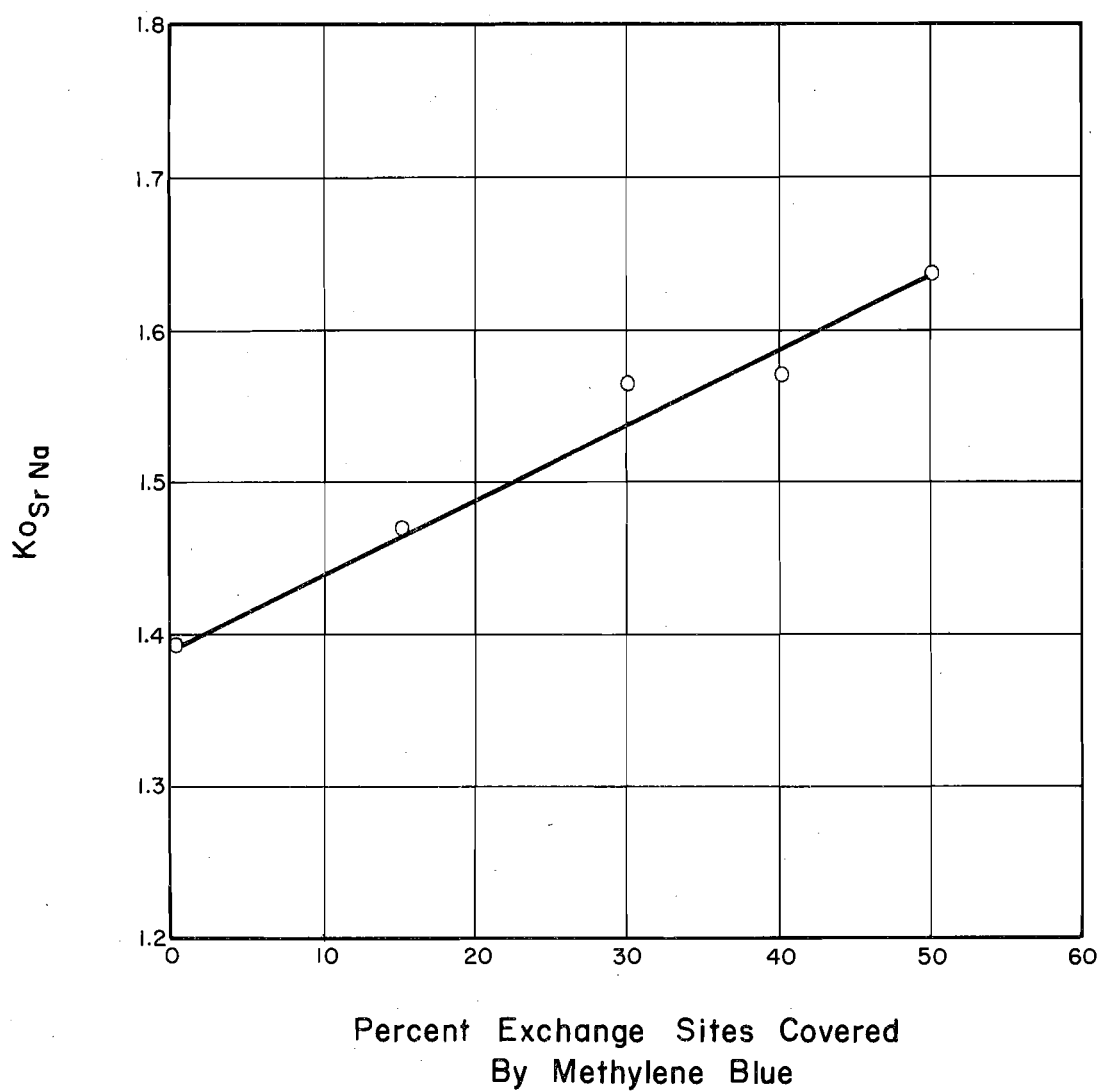


FIG. 29 EFFECT OF METHYLENE BLUE ON ION EXCHANGE EQUILIBRIUM CONSTANTS.

$$m_{\text{Na}}^{\circ} = 1 \times 10^{-2}; \quad m_{\text{Sr}}^{\circ} = 5 \times 10^{-5} - 2 \times 10^{-4}; \quad \text{Na-Illite} = 3.7 \times 10^{-4}$$

	a	b	c
% covered by M.B. ⁺	0	23	46

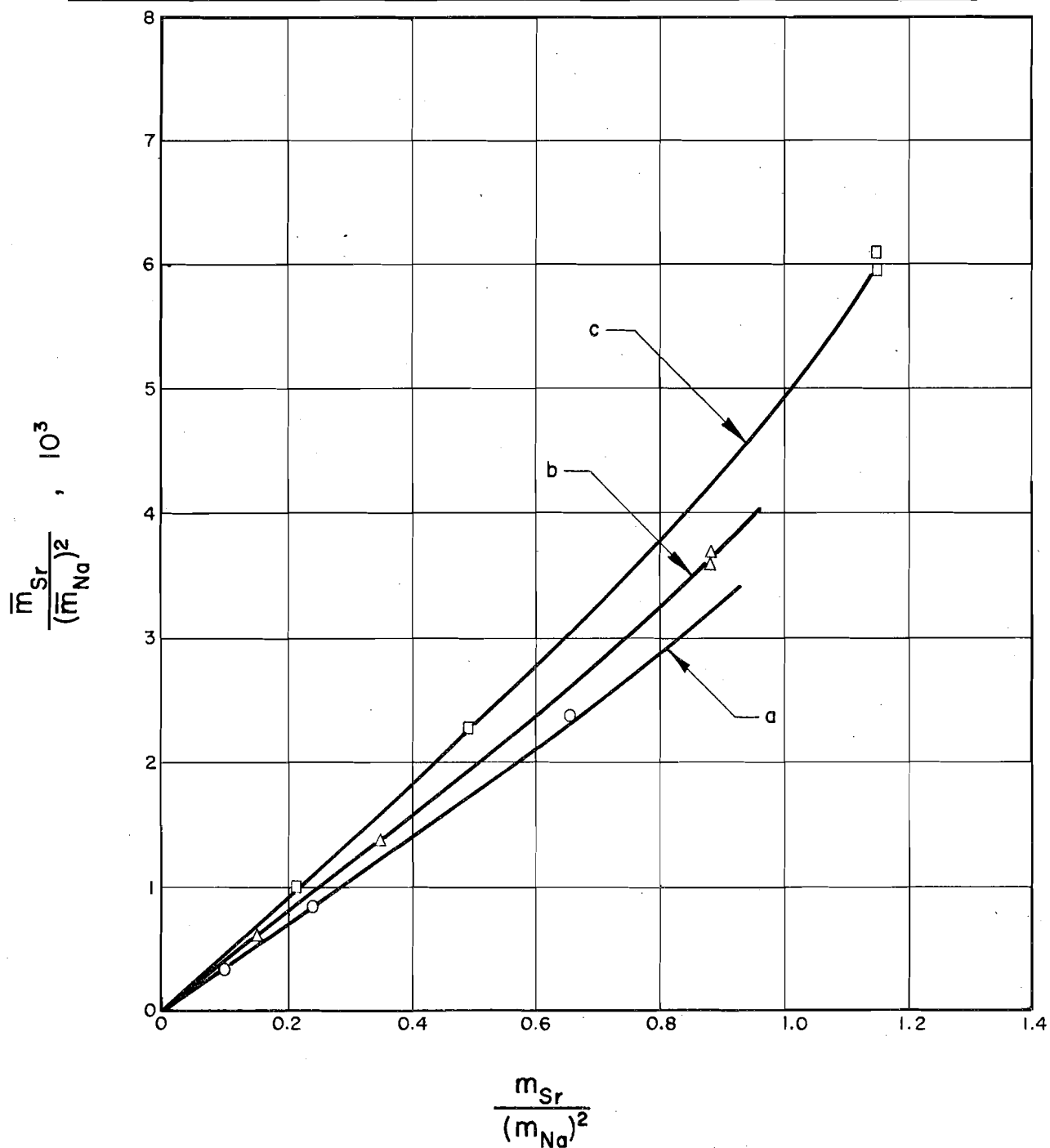


FIG. 30 EFFECT OF METHYLENE BLUE ON EQUILIBRIUM DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Na^+ , FOR Na-ILLITE.

K_{SrNa} are plotted as a function of M.B.^+ adsorption on montmorillonite. In Fig. 30, the values of the counter ion concentration ratio are plotted.

As shown in Figs. 27 and 28, for the counter ion pair $\text{Sr}^{++}\text{-Ca}^{++}$, the presence of M.B.^+ ions in the exchanger phase reduced the amounts of Sr^{++} adsorbed. On the other hand, for the $\text{Sr}^{++}\text{-Na}^+$ pair, the selectivity for Sr^{++} increased as more exchange sites were covered with M.B.^+ ions. The explanation may be that the effects of M.B.^+ result from two different mechanisms, one in which the cover-up effect is involved and the other in which the presence of organic molecules on clay mineral surfaces affect the selectivity of the available exchange sites. In the reaction between Sr^{++} and Ca^{++} , because of their similarity in chemical and physical properties, the effects of the latter mechanism may be insignificant compared to that of the covering-up. In this case, the covering-up and trapping of Ca^{++} ions on clay minerals by M.B.^+ before Sr^{++} addition may result in a higher Ca^{++} concentration in the exchanger phase than its equilibrium value in the absence of M.B.^+ . On the other hand, in the case of $\text{Sr}^{++}\text{-Na}^+$, the effect on the selectivity of clay minerals due to the presence of M.B.^+ ions may have been the dominating factor; therefore, the results show the increase in the selectivity of the clay mineral for Sr^{++} in the presence of M.B.^+ . As will be discussed in the next section, the presence of organic compounds on the exchanger generally increases the selectivity of the clay minerals.

5.2.2. Adsorption of Amine Compounds and Effects on the Clay Ion-Exchange Properties

It has been shown that when certain organic compounds are adsorbed on clay mineral surfaces, it changes the swelling and dispersion

properties of the clay minerals. Jordan⁽³¹⁾ has investigated this matter in great detail. His data show that when aliphatic amine compounds are adsorbed on montmorillonite, their surface properties changed from hydrophilic to hydrophobic. The degree of the change depends on the size and concentration of the adsorbed amine compounds. Jordan, for example, found that when dodecylamine covers all the exchange sites of bentonite its gel volume in water changed from 15 ml per gram to 1 ml per gram.

In the discussion of ion-exchange theory in Section 2.3, it was mentioned that the selective properties of a clay mineral for an inorganic counter ion are closely related to the hydration nature of the cation. Thus, it is evident that when a hydrated inorganic cation comes in contact with the clay surfaces which have been changed to hydrophobic by the organic adsorption, the selectivity of the clay mineral will be different from that of the hydrophilic clay minerals. Glueckauf⁽⁴²⁾ has shown that the sequence of decreasing hydration number of the divalent cations is $\text{Be}^{++} (7.0) > \text{Mg}^{++} (7.0) > \text{Ca}^{++} (5.2) > \text{Sr}^{++} (4.7) > \text{Ba}^{++} (2.0)$, which is in the same sequence as that of the increasing selectivity of the clay exchange media. It is reasonable to assume that the differences in the selectivities of various divalent cations will be increased if the clay exchanger surfaces are to be coated with hydrophobic organic compounds.

Investigations of aliphatic amine adsorption and its effects on the clay ion-exchange properties were conducted using methylamine and dodecylamine. The various experiments with these amines included the reactions carried out to determine (1) the equivalence of the exchange between the amines and Sr^{++} , (2) the relative selectivities of clay minerals for these amines with respect to Sr^{++} ions, and (3) the effects of

the adsorbed amines on the selectivities of clay minerals for the inorganic counter ions, Sr^{++} , Ca^{++} , and Na^+ . The results are summarized in Fig. 31 through Fig. 36.

The equivalence of the exchange between the amines and the Sr^{++} ions was examined by the reactions in which Sr^{++} ions of Sr-clay minerals were leached out by the adsorption of these amines. The experimental results are summarized in Fig. 31, in which the Sr^{++} ions leached out are plotted as a function of the amine adsorption. As shown in Fig. 31, for methylamine, a strict equivalence between the adsorbed amine and the Sr^{++} ions leached out was observed; however, in the case of dodecylamine Sr^{++} leached out was slightly less than the amine adsorption, indicating the adsorption of dodecylamine may involve non-ionic type adsorption in addition to the cationic adsorption. The nature of the equivalence of the exchange between the amine and Sr^{++} was independent of the type of clay mineral. The same results were observed for both montmorillonite and illite.

The equivalence of the amine adsorption and the counter ion elution indicates that the adsorption of these amines was primarily exchange adsorption. In order to determine the relative selectivity of the clay minerals for these amines with respect to Sr^{++} ions, the exchange reactions between Sr^{++} and the amines were studied with both montmorillonite and illite. The results are summarized in Figs. 32 through 36. In Figs. 32 and 33 the exchange adsorption of methylamine and dodecylamine on montmorillonite and illite are presented. The amounts of the adsorbed amines are plotted as a function of total amine concentration in the presence of various counter ions. In Fig. 32, line "a" represents

(a) Methylamine, (b) Dodecylamine, (c) Arginine

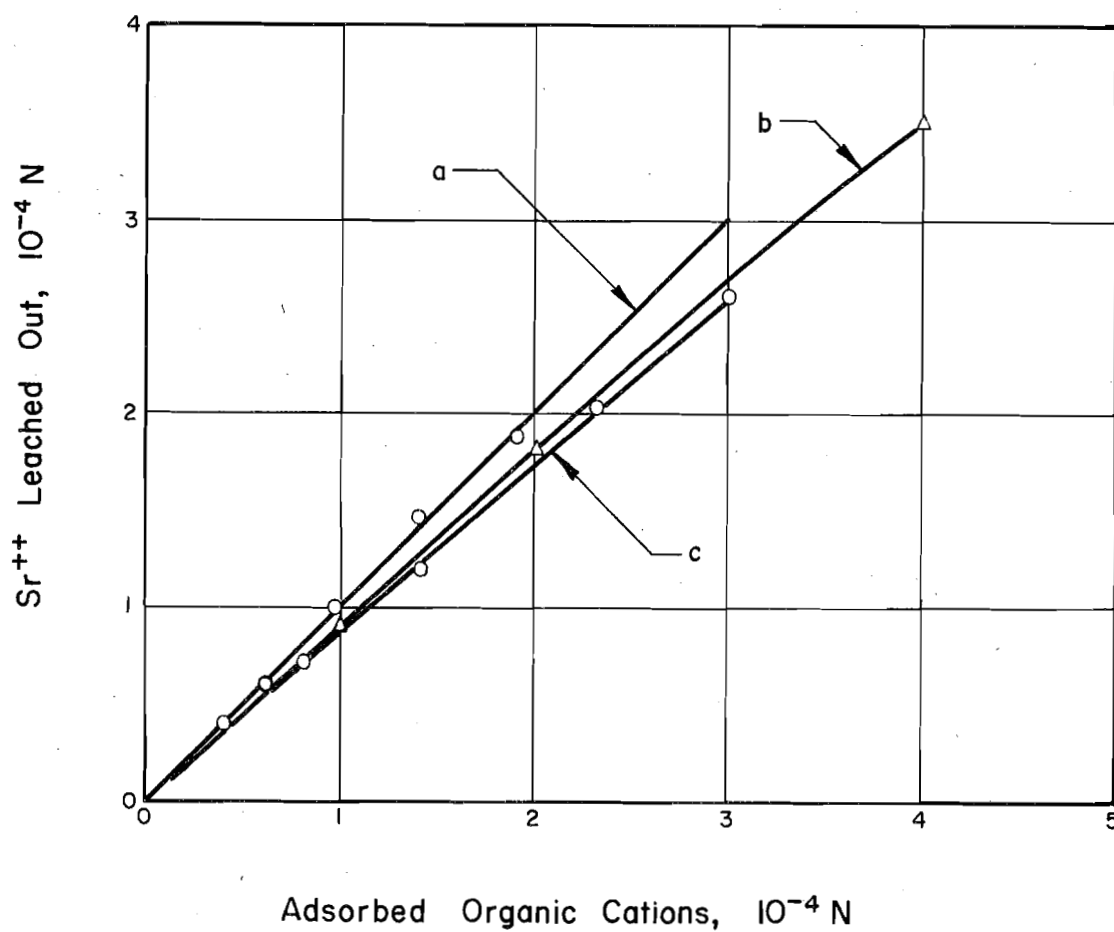


FIG. 31 Sr^{++} LEACHING FROM Sr-CLAY BY ORGANIC CATIONS.

	Organic Cations	Sr ⁺⁺	Other	Clay Minerals, N
a,	Dodecylamine	1×10^{-3}	0	Sr-Mont.= 7.9×10^{-4}
b,	Methylamine	0	0	" "
c,	Methylamine	1×10^{-4}	0	" "
d,	Methylamine	1×10^{-3}	0	" "
e,	Arginine	2×10^{-4}	0	" "
f,	Arginine	2×10^{-4}	Mg ⁺⁺ = 4×10^{-4}	" "
g,	Arginine	4×10^{-4}	Na ⁺ = 1×10^{-2}	Na-Mont.= 5.0×10^{-4}

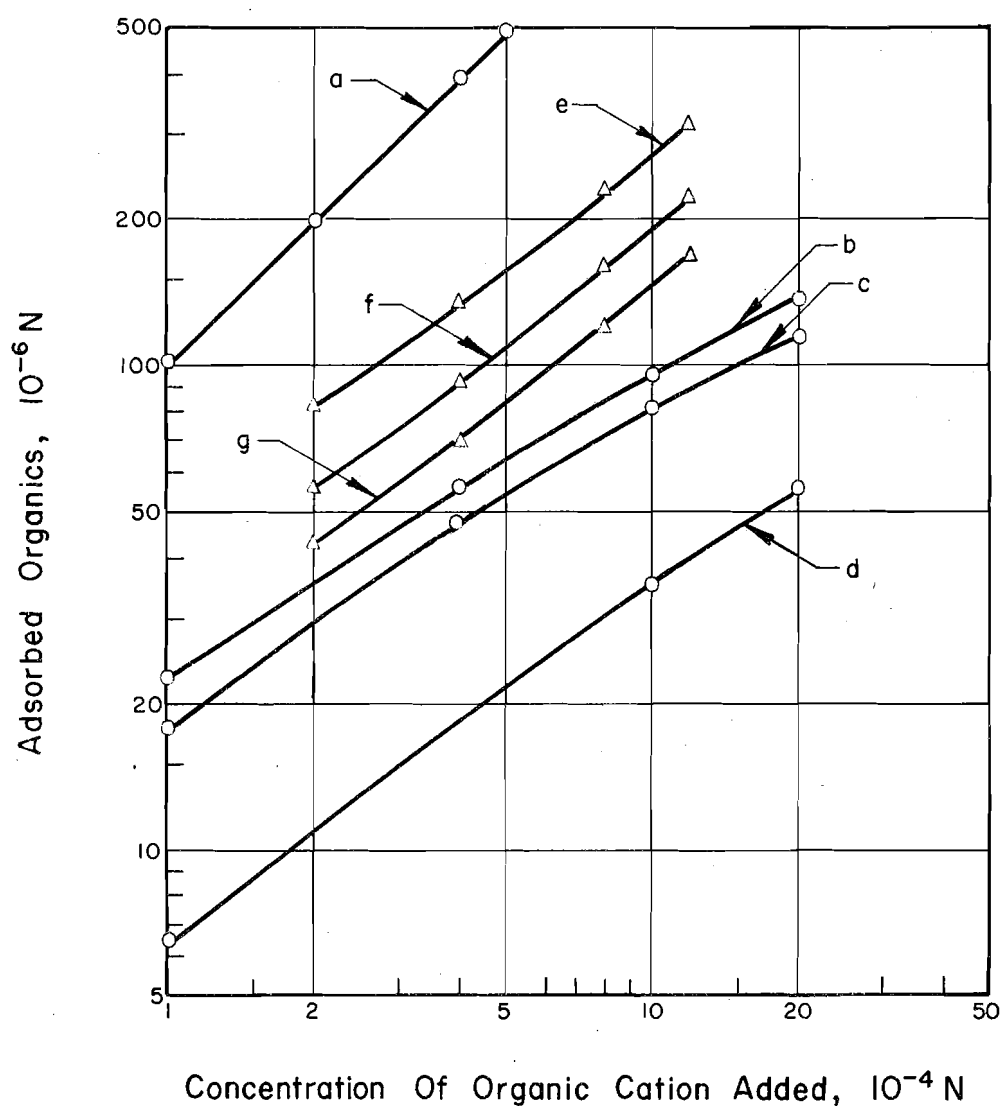


FIG. 32 ADSORPTION OF ORGANIC CATION ON MONTMORILLONITE.

	Organic Cations	Sr ⁺⁺	Other	Clay Minerals
a,	Arginine	2×10^{-4}	$\text{Na}^+ = 1 \times 10^{-2}$	$\text{Na-Illite} = 8.5 \times 10^{-4}$
b,	Arginine	1×10^{-4}	$\text{Mg}^{++} = 4 \times 10^{-4}$	$\text{Sr-Illite} = 3.5 \times 10^{-4}$
c,	Methylamine	5×10^{-5}	0	$\text{Sr-Illite} = 2.0 \times 10^{-4}$
d,	Methylamine	5×10^{-4}	0	$\text{Sr-Illite} = 2.0 \times 10^{-4}$

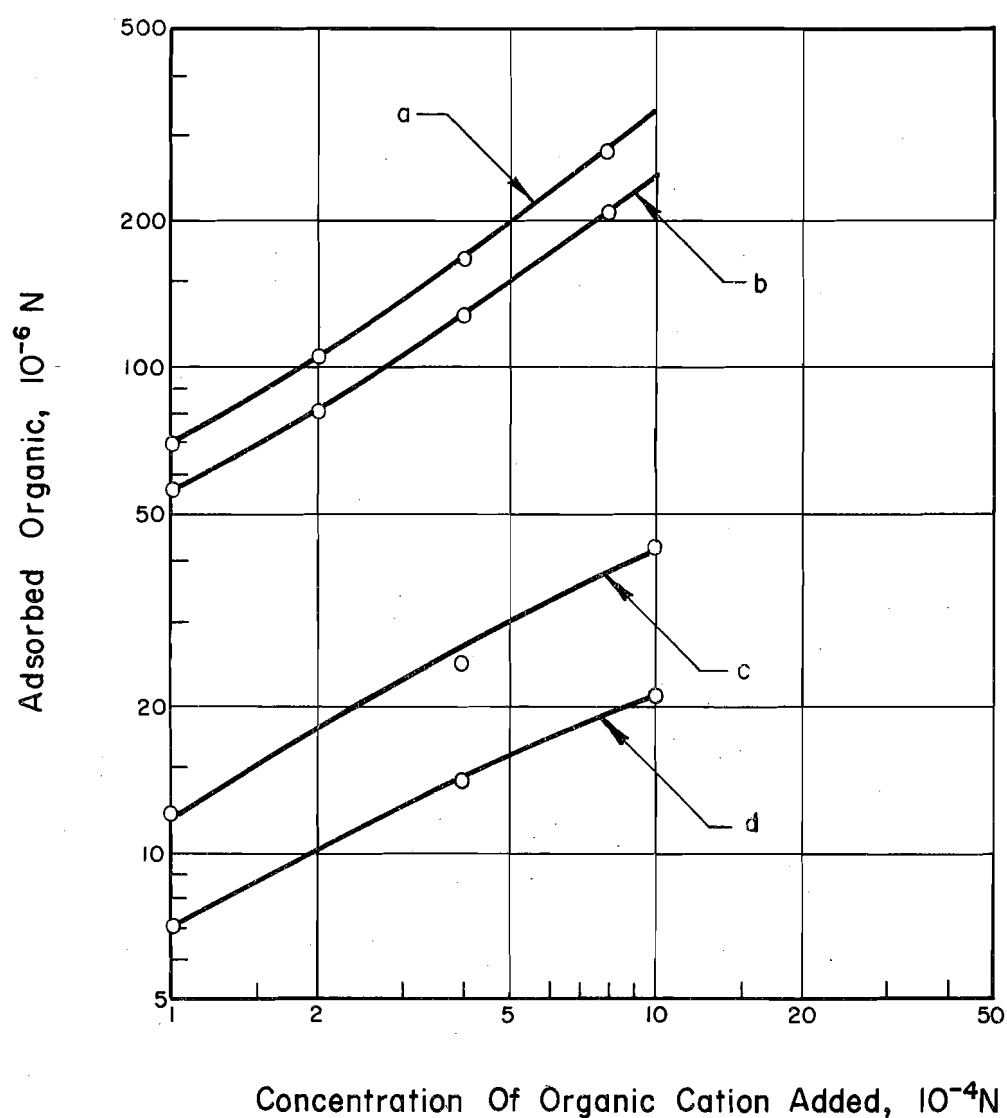


FIG. 33 ADSORPTION OF ORGANIC CATION ON ILLITE.

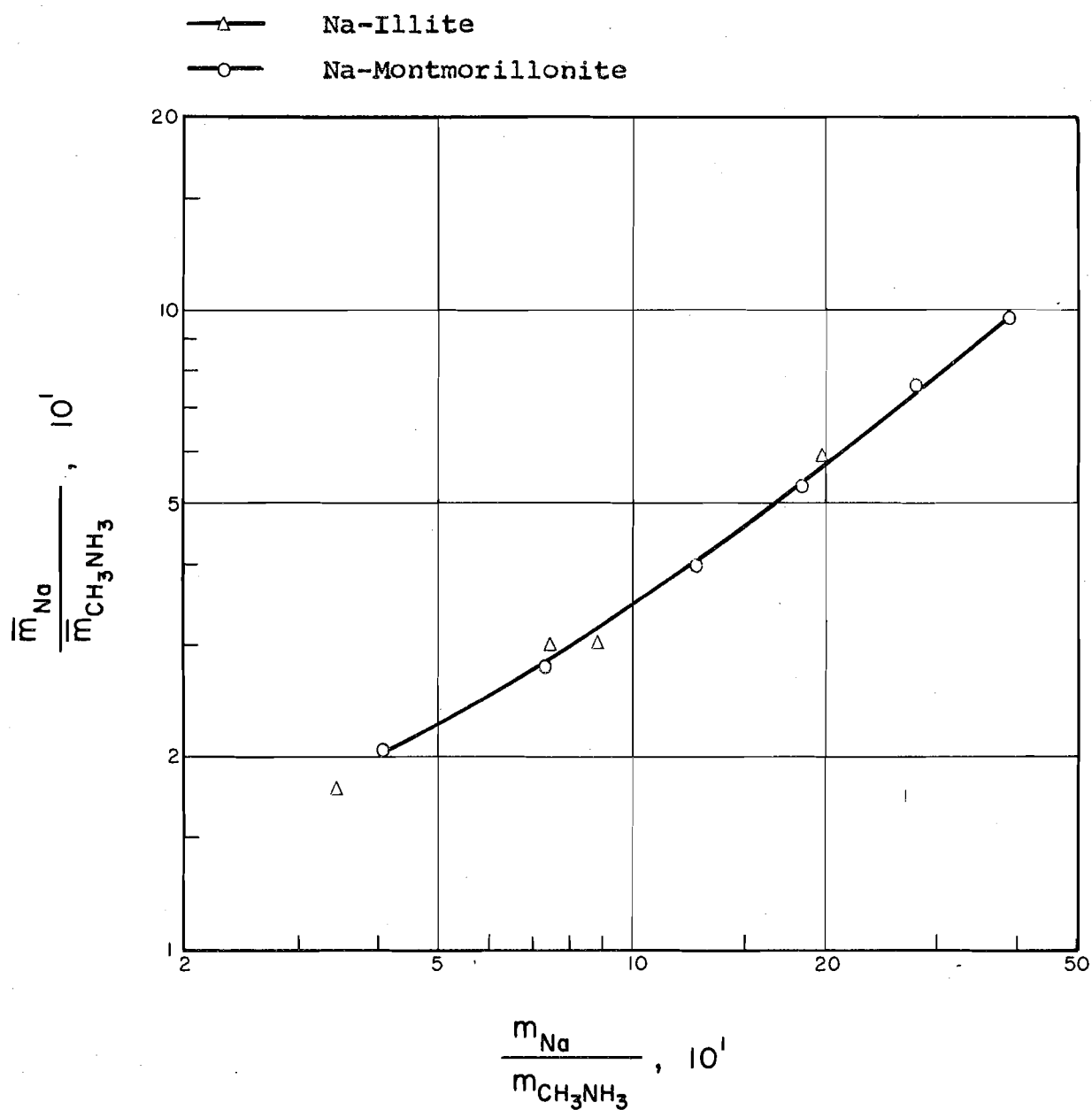


FIG. 34 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH Na^+ , METHYLAMINE, AND CLAY MINERALS.

	a	b	c
Organic Cation	methylamine	methylamine	arginine
Clay Minerals	Sr-Mont.	Sr-Illite	Sr-Mont.

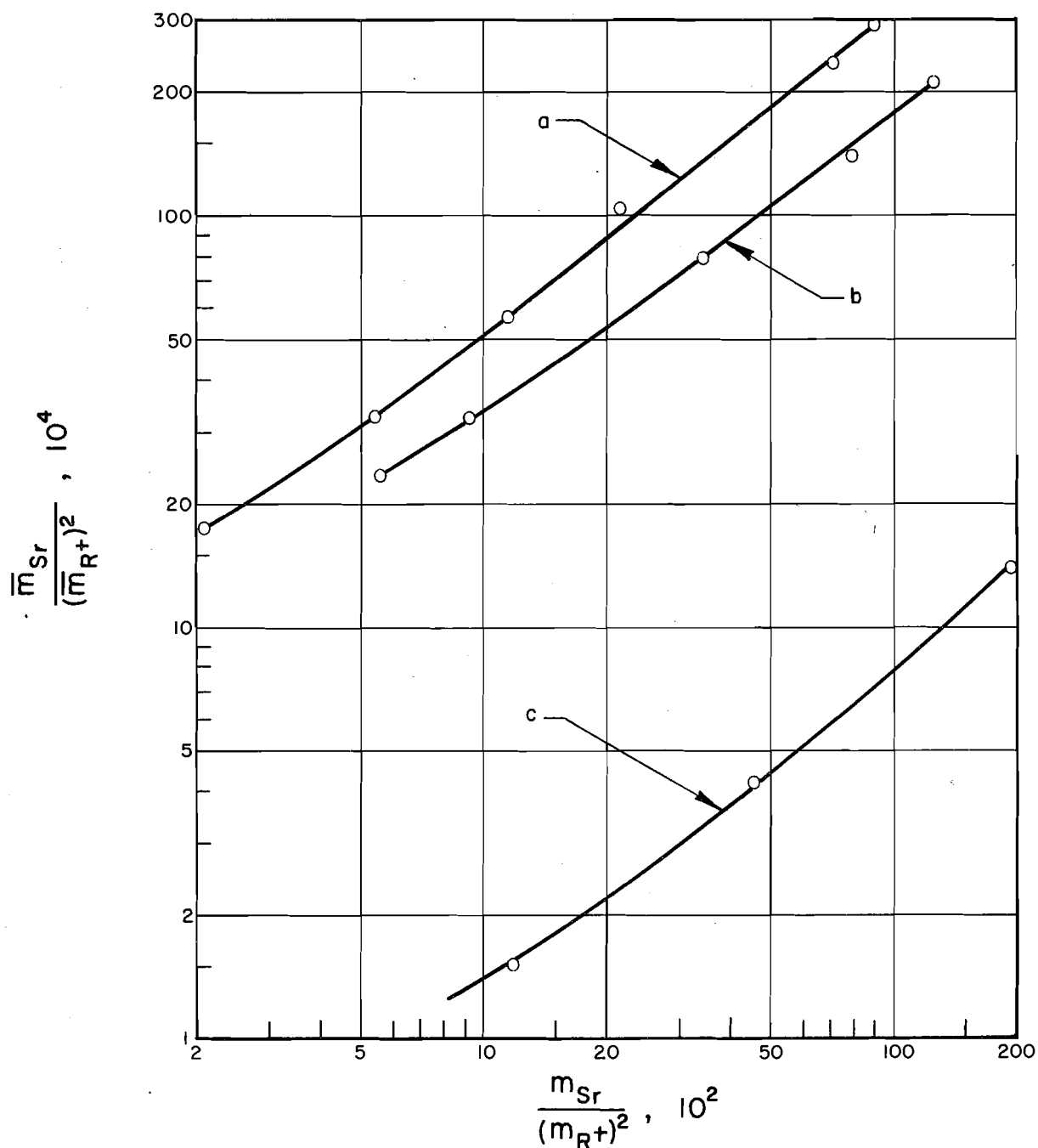


FIG. 35 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH Sr^{++} , ORGANIC CATIONS, AND CLAY MINERALS.

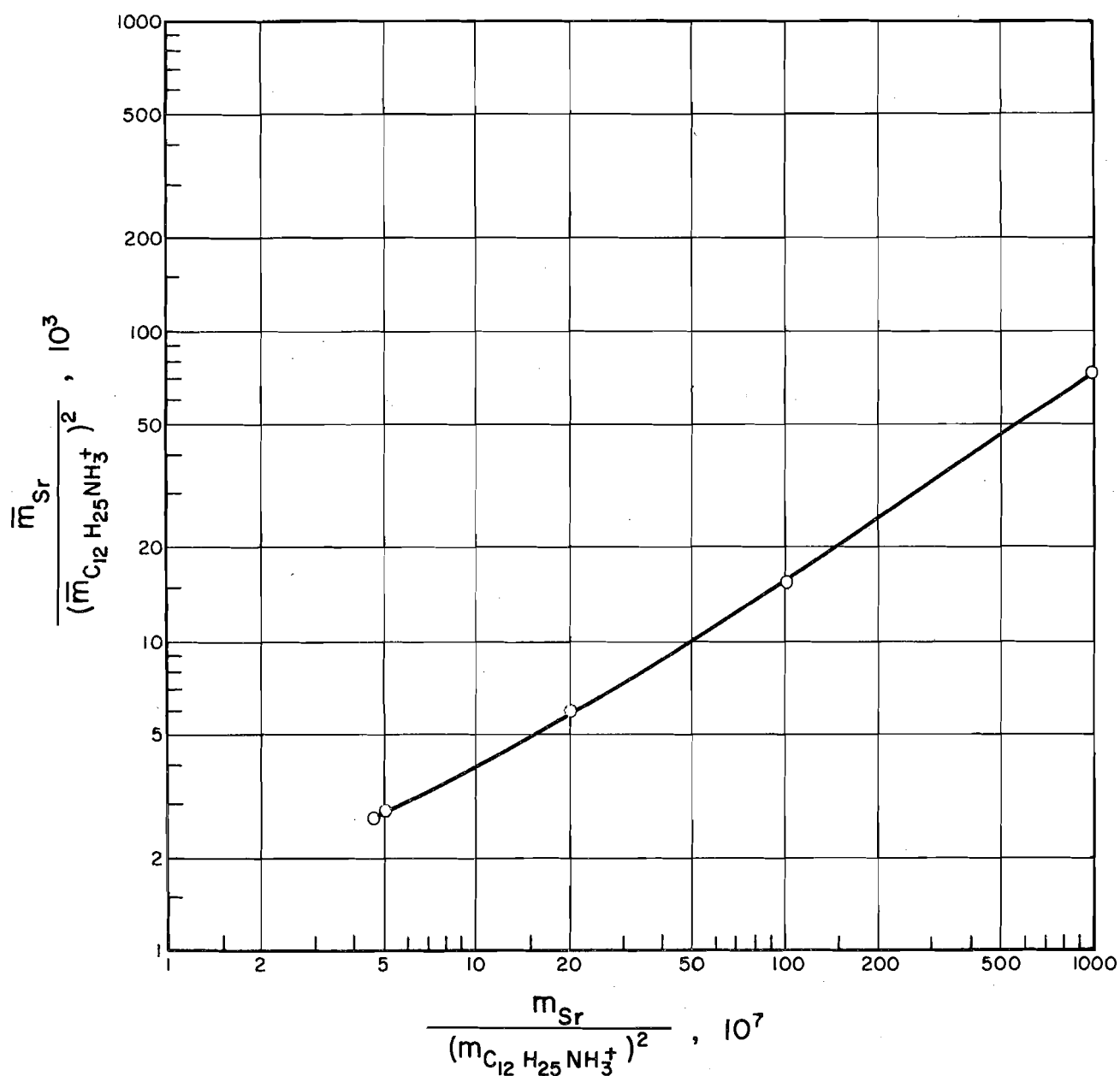


FIG. 36 EQUILIBRIUM DISTRIBUTION OF COUNTER IONS IN A SYSTEM WITH Sr^{++} , DODECYLAMINE, AND MONTMORILLONITE.

complete adsorption of dodecylamine. All others represent about 10 to 50% of the organic adsorptions. Complete adsorption was not attained for arginine or methylamine on either the montmorillonite or the illite. The adsorption data of methylamine and dodecylamine were also analyzed in terms of ion-exchange equilibrium reactions between the organic cations and the inorganic cations. The results of the exchange reactions between methylamine and Na^+ are shown in Fig. 34, in which the ratios of the counter ion concentrations in the exchanger phase are plotted as a function of the ratios in the solution phase. Similarly the results of the exchange reactions between Sr^{++} and the organic cations are shown in Figs. 35 and 36. The ratio of the ordinate to abscissa values is the mass-action equilibrium constant without the activity corrections.

Comparing Figs. 34, 35, and 36, with those of Section 4.4 (Fig. 5 through Fig. 12), it is evident that for the counter ion pairs involving the organic cations, the mass-action equilibrium expression is not satisfactory for describing the ion-exchange reactions. The value of the mass-action equilibrium constants depended on the experimental conditions. The equilibrium constants computed from the data shown in Figs. 34, 35, and 36 are summarized in Table 14. As shown in Table 14, for both methylamine and dodecylamine, the selectivity of clay minerals for the organic cations decreased as more of the organic cations were adsorbed on the clay minerals, which indicates that the affinity for organic cations decreases as more of the organic cations occupy the exchange sites. A similar phenomenon has been observed in the exchange reactions involving hydrogen ions (Section 4.3). As shown in Table 14, the selectivity of clay minerals was much higher for a large organic

TABLE 14
EQUILIBRIUM CONSTANTS FOR THE EXCHANGE BETWEEN INORGANIC AND ORGANIC CATIONS

Inorganic Cation (A^{a+})	Concentration range, N		Clay	$\frac{(\bar{m}_A)}{(\bar{m}_R)^a}$	Ko_{AR}	Figure Number
	Organic Cation (R^+)					
Na^+ 10^{-3} - 2×10^{-3}	methylamine 10^{-5} - 5×10^{-5}		Na-Mont.	1.00×10^2	2.5×10^{-1}	34
			5.0×10^{-4}	2.00×10^1	5.0×10^{-1}	
Na^+ 5×10^{-4}	methylamine 4×10^{-6} - 4×10^{-5}		Na-Illite	5.5×10^1	2.75×10^{-1}	34
			1.07×10^{-4}	1.8×10^1	5.0×10^{-1}	
Sr^{++} 10^{-3} - 2×10^{-3}	methylamine 4×10^{-4} - 3×10^{-3}		Sr-Mont.	3×10^6	3.34×10^2	35a
			7.5×10^{-4}	1.7×10^5	8.5×10^2	
Sr^{++} 1.0×10^{-4} - 5×10^{-4}	methylamine 1×10^{-4} - 1×10^{-3}		Sr-Illite	2.2×10^6	1.8×10^2	35b
			2.0×10^{-4}	2.3×10^5	4.1×10^2	
Sr^{++} 2×10^{-4}	arginine 2×10^{-4} - 1×10^{-3}		Sr-Mont.	1.4×10^5	7.0	35c
			7.9×10^{-4}	1.5×10^4	12.5	
Sr^{++} 1×10^{-3}	dodecylamine 1.0×10^{-4} - 4×10^{-4}		Sr-Mont.	7.5×10^5	7.4×10^{-6}	36
			7.9×10^{-4}	2.8×10^4	5.6×10^{-4}	

cation, which probably resulted from the fact that in the case of a large organic cation the Van der Waals forces are also involved in addition to the coulombic force. The selectivity of clay minerals for dodecylamine is so strong that the adsorption is practically irreversible, as it was also in the case of methylene blue.

In order to examine the effects of the adsorbed organic cations on the selective properties of the available exchange sites, ion-exchange reactions between the counter ion pairs $\text{Sr}^{++}\text{-Ca}^{++}$ and $\text{Sr}^{++}\text{-Na}^+$ were performed with clay minerals whose exchange sites were partially covered with organic cations. The results are shown in Figs. 37, 38, 39, and 40. In Fig. 37, the results of the exchange reactions between Sr^{++} and Ca^{++} with montmorillonite whose exchange sites are partially covered with methylamine (0-22%) are presented. In Figs. 38, 39, and 40, the results of the exchange reactions between the counter ion pairs $\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$, and $\text{Sr}^{++}\text{-Na}^+$ in equilibrium with montmorillonite, whose exchange sites are partially covered with dodecylamine, are presented. As shown in Fig. 37, for methylamine adsorption, no significant effects on the equilibrium constants were observed. On the other hand, in the case of dodecylamine adsorption, the equilibrium constants increased as more of the exchange sites were covered by dodecylamine. The effects of dodecylamine are greater for the counter ion pair whose equilibrium constant is further from unity; that is the effects are much higher for $\text{Sr}^{++}\text{-Na}^+$ than for $\text{Sr}^{++}\text{-Ca}^{++}$. This is probably due to the fact that in the case of the counter ion pair $\text{Sr}^{++}\text{-Ca}^{++}$, the chemical and physical properties of these ions are so similar that the effects of the organic may have been about the same. In the case of $\text{Sr}^{++}\text{-Na}^+$ pair, however, the effects are much higher due to the differences in their properties.

(a) Kd_{Sr} ; (b) Kd_{Ca} ; (c) Ko_{SrCa}

$m_{Sr}^0 = 6 \times 10^{-6}$; $m_{Ca}^0 = 5 \times 10^{-4}$; $Ca\text{-}Mont. = 8.0 \times 10^{-4} N$

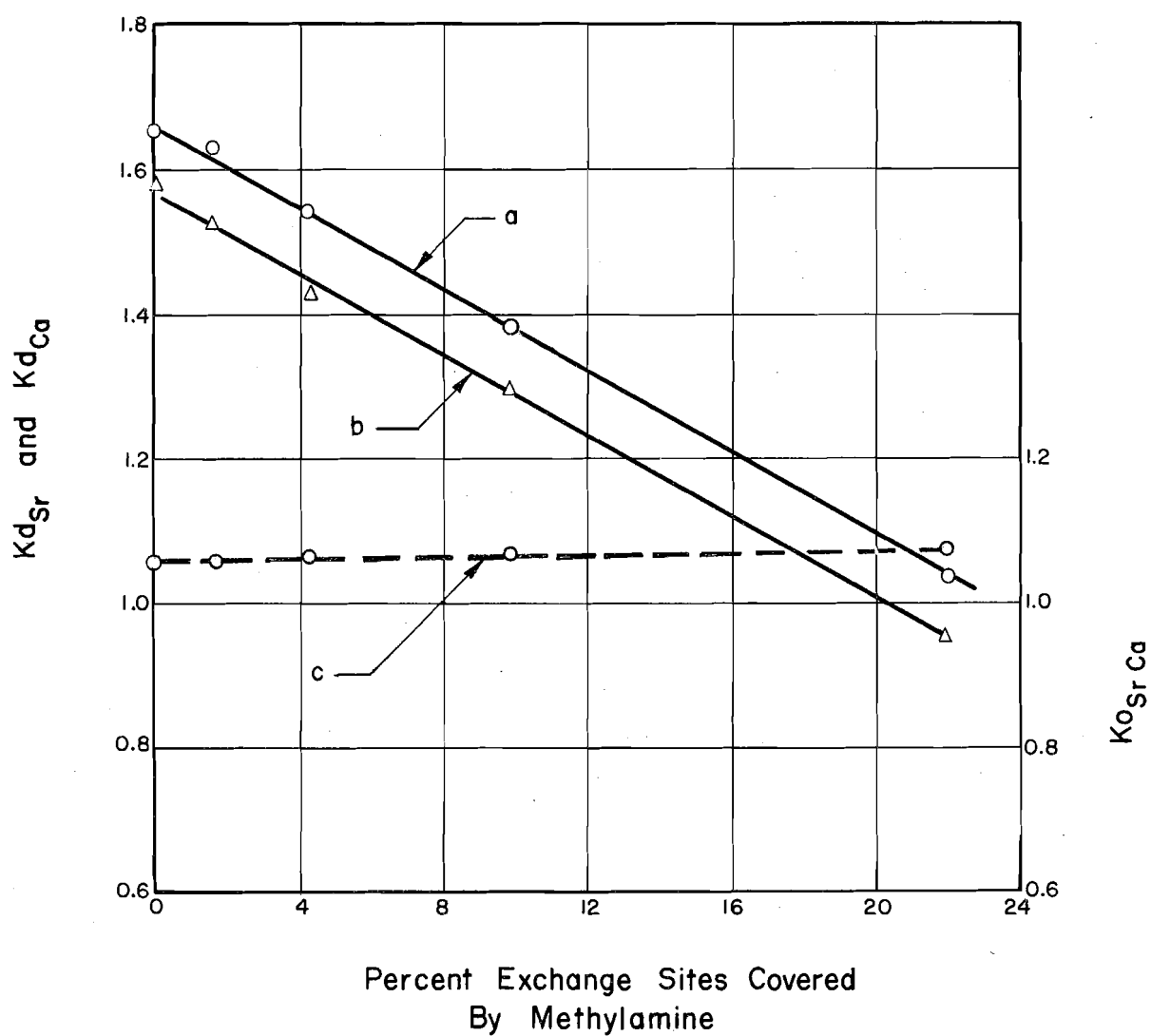


FIG. 37 EFFECTS OF ADSORBED METHYLAMINE ON DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Ca^{++} .

(a) Kd_{Sr} ; (b) Kd_{Ca} ; (c) Ko_{SrCa}

$m_{Sr}^o = 1 \times 10^{-4}$; $m_{Ca}^o = 1 \times 10^{-3}$; $Sr-Mont. = 7.9 \times 10^{-4} N$

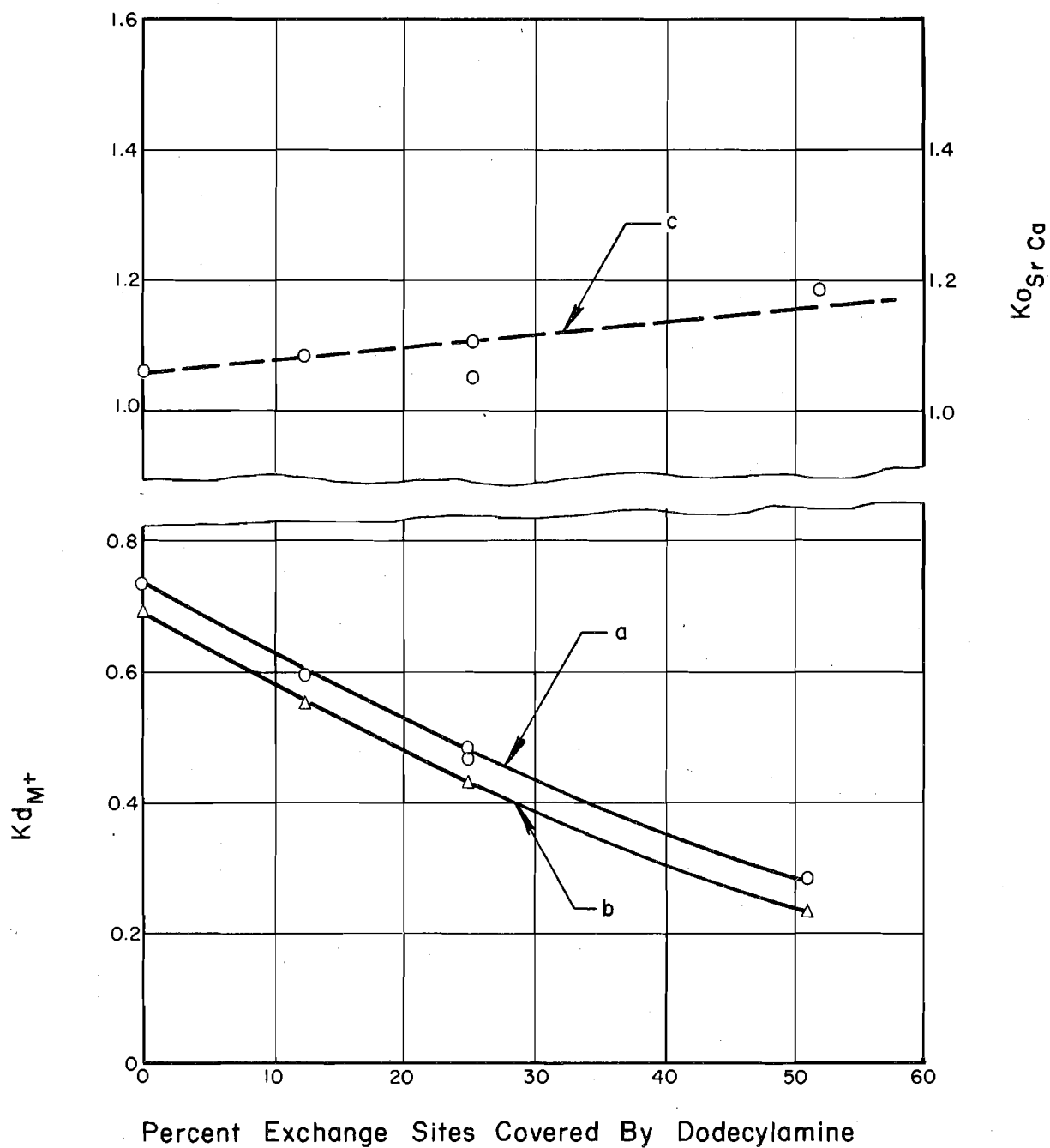


FIG. 38 EFFECTS OF ADSORBED DODECYLAMINE ON DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Ca^{++} .

$$(a) K_{O_{SrMg}} = \frac{K_{d_{Sr}}}{K_{d_{Mg}}} = \frac{(a-1)}{(a-2)} ; \quad (b) K_{O_{SrMg}} = \frac{(b-1)}{(b-2)}$$

	Mg ⁺⁺	Sr ⁺⁺	Sr-Mont., N
a	1x10 ⁻³	2x10 ⁻⁴	7.3x10 ⁻⁴
b	1x10 ⁻³	4x10 ⁻⁴	7.3x10 ⁻⁴

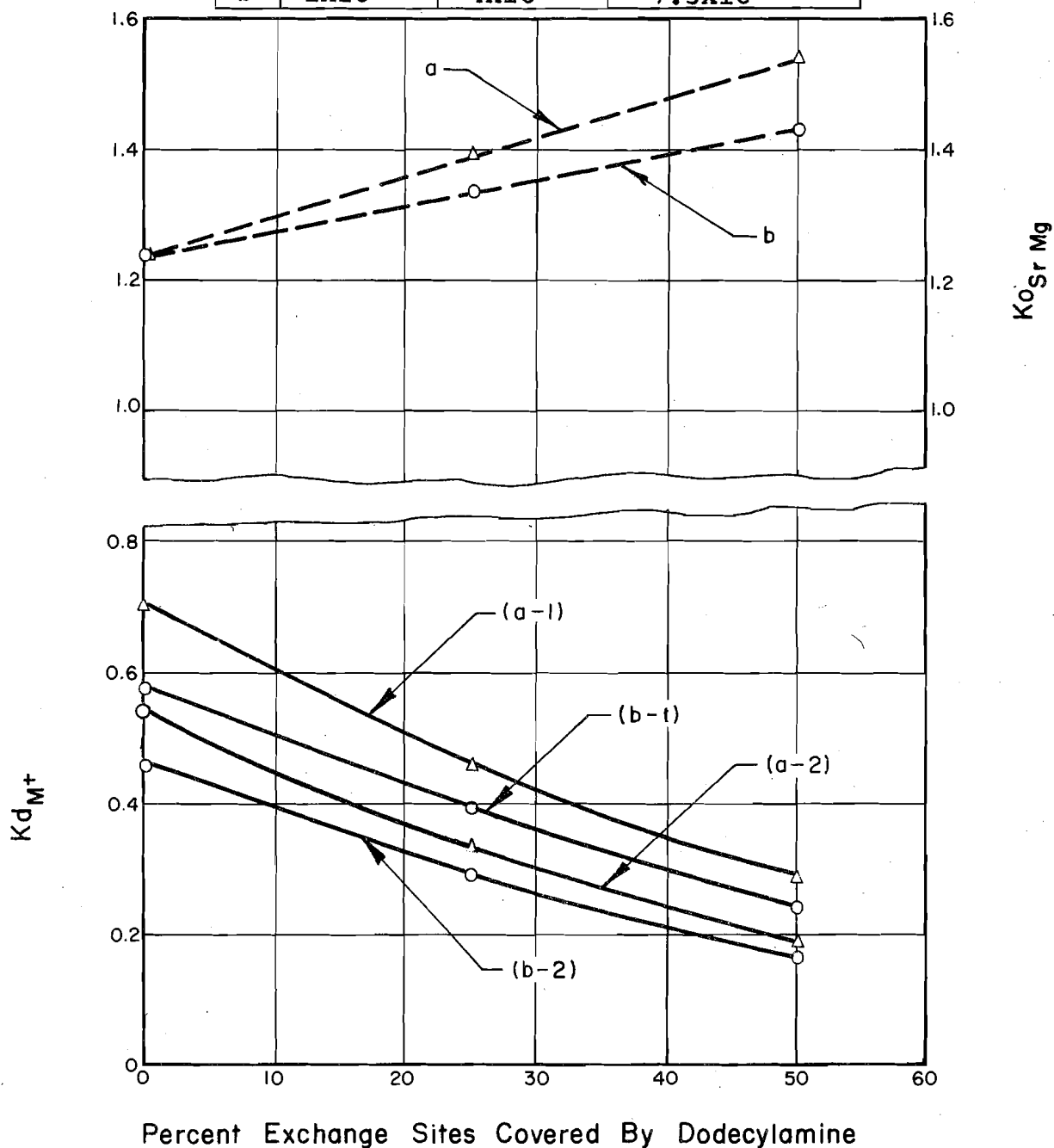


FIG. 39 EFFECTS OF ADSORBED DODECYLAMINE ON DISTRIBUTION OF COUNTER IONS, Sr⁺⁺ AND Mg⁺⁺.

(1) $K_{O_{SrNa}}$ for a; (2) $K_{O_{SrNa}}$ for b

	Na^+	Sr^{++}	Na-Mont., N
a,	1×10^{-2}	2×10^{-4}	Na-Mont. = 7.4×10^{-4}
b,	1×10^{-2}	4×10^{-4}	Na-Mont. = 7.4×10^{-4}

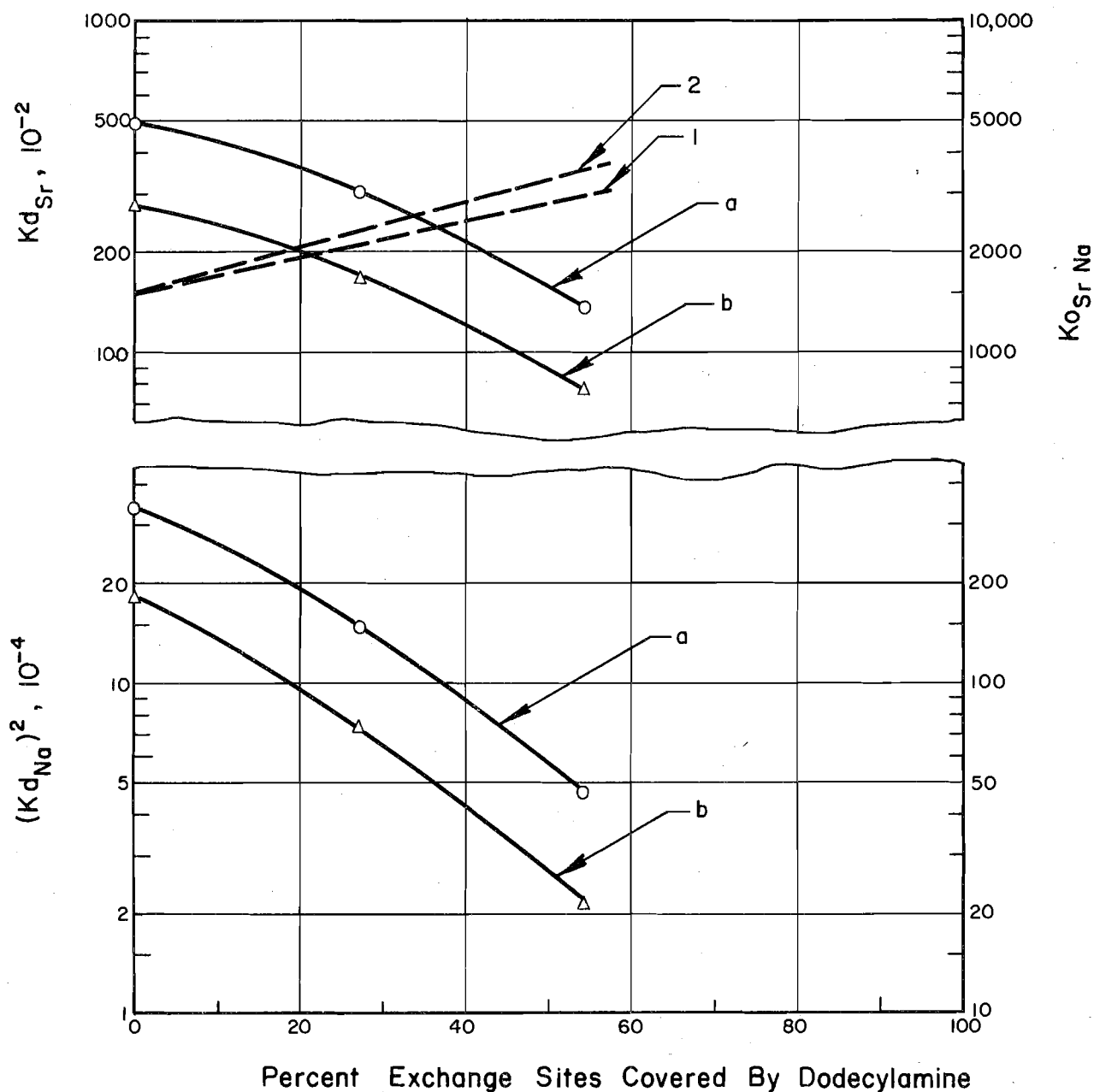


FIG. 40 EFFECT OF ADSORBED DODECYLAMINE ON DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Na^+ .

5.2.3. Adsorption of Arginine and Effects on the Clay Ion-Exchange Properties

The adsorption of polycationic organic compounds and its probable effects on soil ion-exchange properties were discussed in Section 2.6.2.2. Arginine, which is accepted as a naturally occurring amino acid⁽⁴³⁾, was used to study adsorption on clay minerals and its effects on the ion-exchange properties of clay minerals.

The experiments were performed in a similar manner to those for the amine compounds. The equivalence of the arginine adsorption and Sr^{++} elution from Sr-clay minerals are shown in Fig. 31, and the adsorption of arginine on montmorillonite and illite is shown in Fig. 32 and Fig. 33, respectively. The selectivities of montmorillonite for arginine with respect to Sr^{++} ions are shown in Fig. 35 (curve c) and in Table 14. The effects of the adsorbed arginine on the soil ion-exchange properties were examined from the exchange reactions between the cation pairs $\text{Sr}^{++}\text{-Ca}^{++}$, $\text{Sr}^{++}\text{-Mg}^{++}$, and $\text{Sr}^{++}\text{-Na}^{+}$ in equilibrium with the clay minerals whose exchange sites were partially covered with arginine. The results are summarized in Figs. 41, 42, and 43.

As shown in Figs. 41 and 42, the effects were similar to those of methylamine and dodecylamine. The degree of the effects was much lower than with dodecylamine and slightly higher than with methylamine. The effect of arginine was about the same for both montmorillonite (Fig. 42) and illite (Fig. 43), which indicates that the change in the expanding properties of the clay minerals are not involved in these effects. The effect of arginine was probably due to the same mechanism involved in the effect of the amine compounds. It is uncertain whether

(a) Kd_{Sr} ; (b) Kd_{Mg} ; (c) Ko_{SrMg}

$m_{Sr}^o = 2 \times 10^{-4}$; $m_{Mg}^o = 4 \times 10^{-4}$; $Sr-Mont. = 7.9 \times 10^{-4} N$

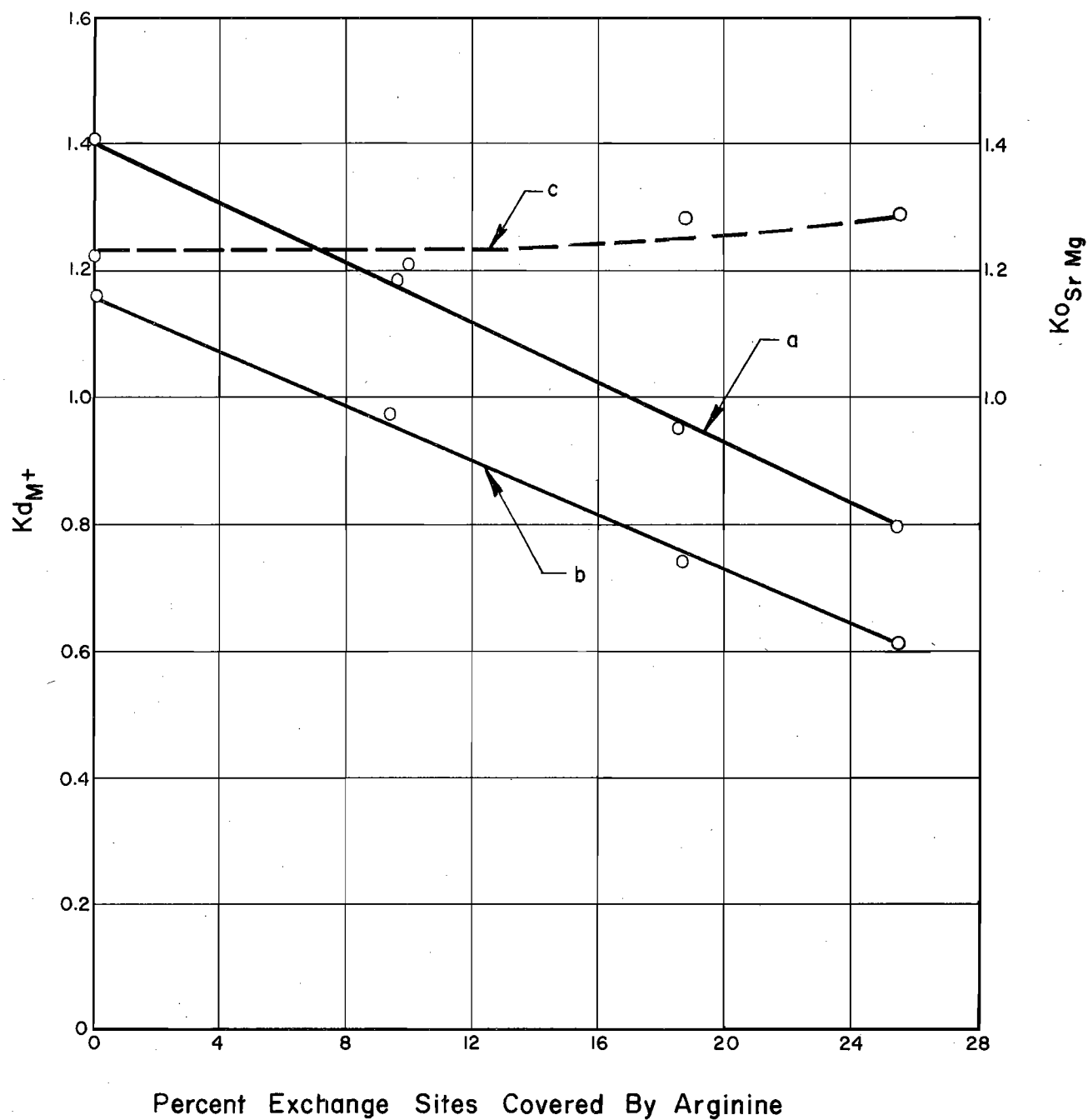


FIG. 41 EFFECTS OF ADSORBED ARGININE ON DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Mg^{++} .

(a) Kd_{Sr} ; (b) $(Kd_{Na})^2$; (c) Ko_{SrNa}

$m_{Sr}^o = 4 \times 10^{-4}$; $m_{Na}^o = 1 \times 10^{-2}$; Na-Mont. = $5.0 \times 10^{-4} N$

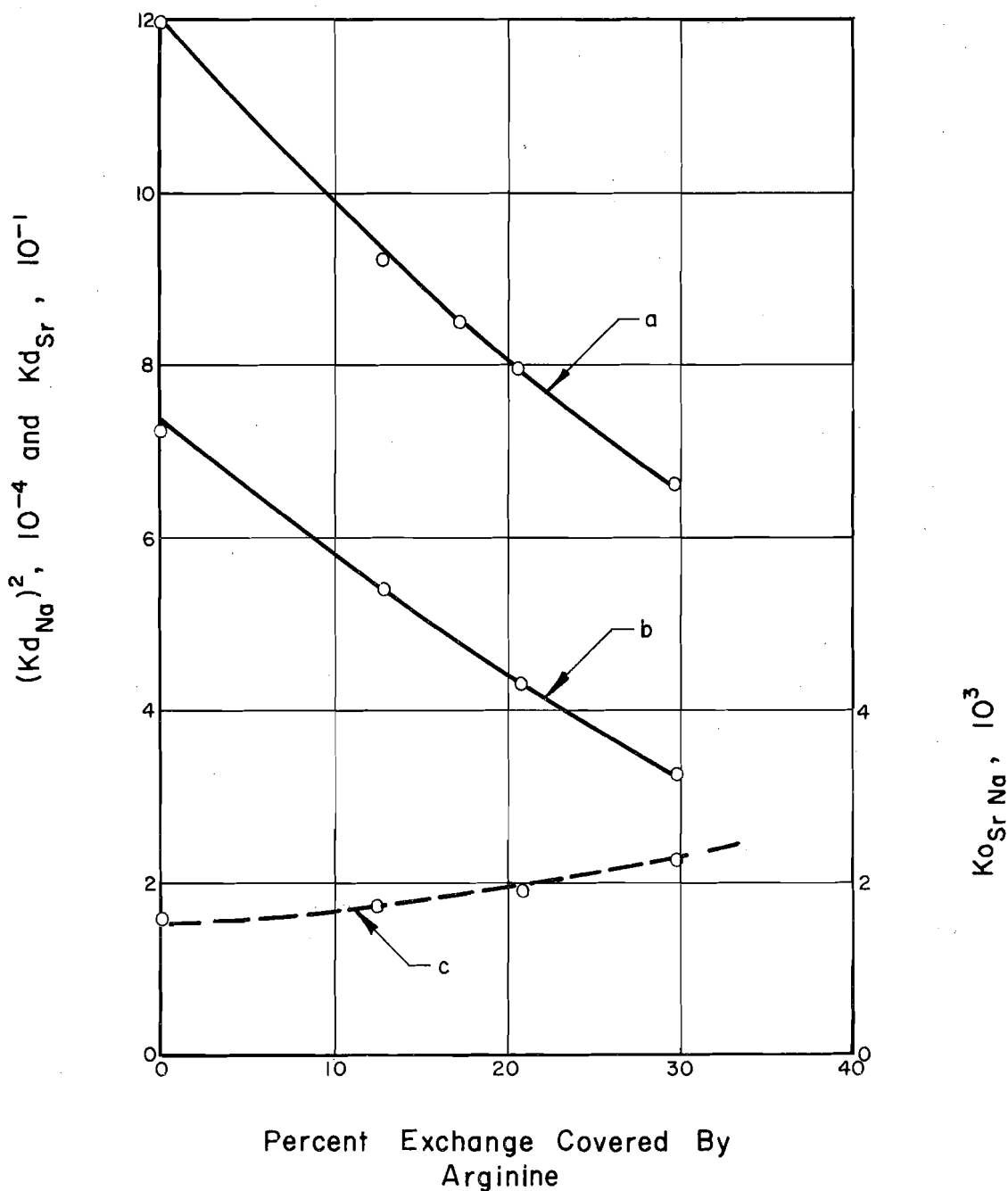


FIG. 42 EFFECTS OF ADSORBED ARGININE ON DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Na^+ WITH MONTMORILLONITE.

(a) Kd_{Sr} ; (b) $(Kd_{Na})^2$; (c) Ko_{SrNa}

$m_{Sr}^0 = 2 \times 10^{-4}$; $m_{Na}^0 = 10^{-2}$; Na-Illite $= 5.7 \times 10^{-4}$

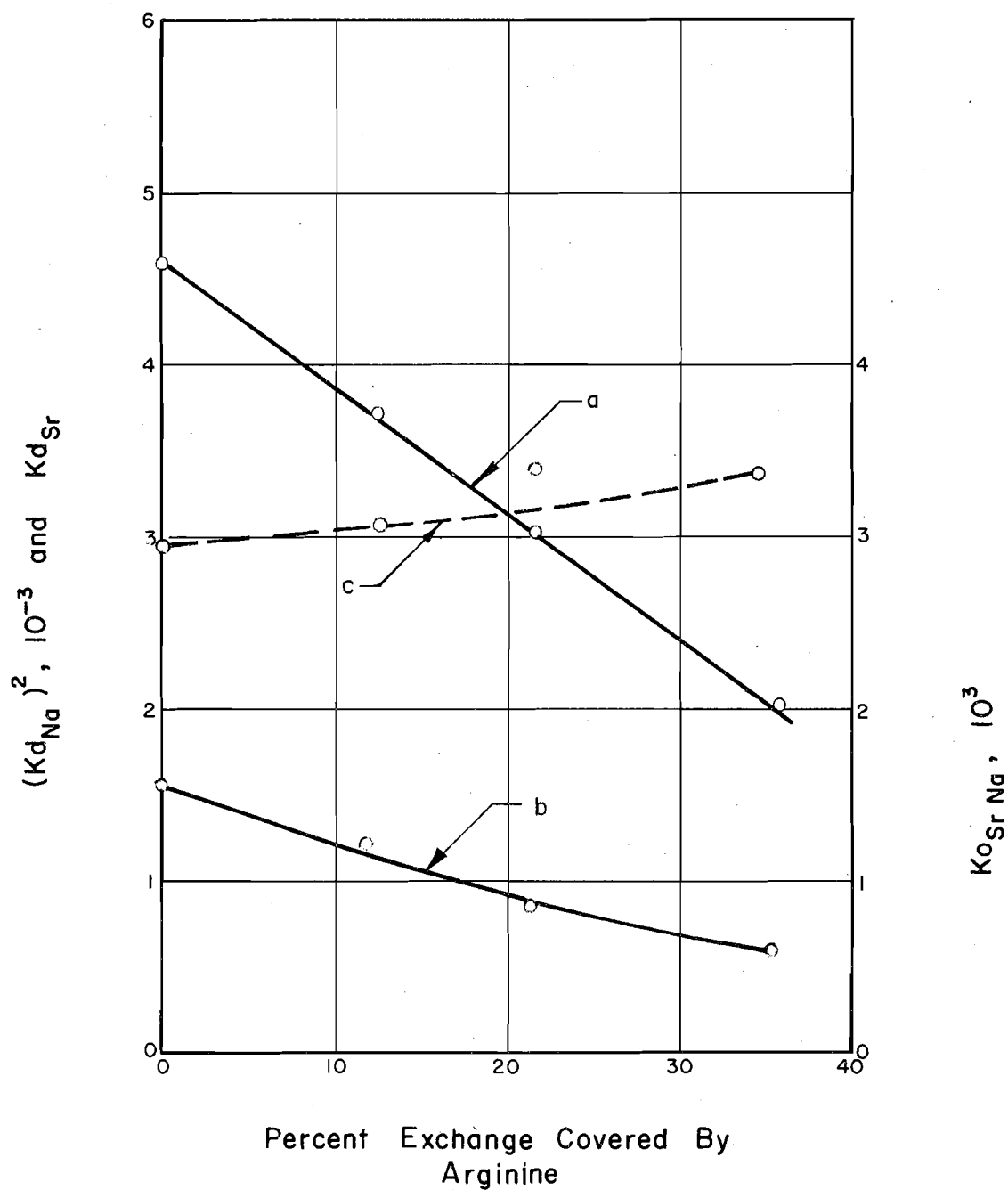


FIG. 43 EFFECTS OF ADSORBED ARGININE ON DISTRIBUTION OF COUNTER IONS, Sr^{++} AND Na^+ WITH ILLITE.

the bridging effects by the adsorption of arginine on two facing surfaces of the basal planes actually occurred or not. From the ionization constants of arginine (Table 3), it seems that the ionization of the second amine group ($pK_a = 2.17$) had not occurred, and hence it is more probable that the bridging effects had not occurred.

5.2.4. Adsorption of Sucrose and Effects on the Clay Ion-Exchange Properties

Attempts to study the effects of sucrose on soil ion-exchange properties were unsuccessful, because regardless of the concentration of sucrose, no adsorption was observed. Furthermore, the presence of sucrose in the solution phase had no effect on the ion-exchange equilibrium between various inorganic counter ion pairs. The exchange reaction between the counter ion pairs $Sr^{++}-Ca^{++}$, $Sr^{++}-Mg^{++}$, and $Sr^{++}-Na^+$ in the presence of sucrose up to 2×10^{-3} N in the solution phase had no effect on the distribution of these cations.

Summarizing the experimental findings concerning organic adsorption and its effects on clay ion-exchange properties, it can be concluded that certain organic compounds are quite capable of reducing the exchange capacities of clays and also affect their selective properties. Adsorption of large organic cations such as dodecylamine and methylene blue is an irreversible reaction, and hence the adsorption of these organic molecules causes reduction of the exchange capacities. On the basis of the experimental results with methylamine, arginine, dodecylamine and methylene blue, it is evident that larger organic cations are more strongly adsorbed on clay surfaces, indicating the involvement of

Van der Waals forces between the organic chain and the clay surfaces in addition to the coulombic forces.

The investigations of the effects of adsorbed organic compounds on soil ion-exchange properties show that the adsorption of large organic molecules, such as dodecylamine and methylene blue, do indeed affect the ion-exchange properties by covering-up the exchange sites or by the change of the clay mineral surface from hydrophilic to hydrophobic. The effects of organic adsorption depend on the natures, concentrations, and sizes of the organic compounds. The comparison of the results of methylene blue and dodecylamine indicates that with methylene blue, which is less hydrophobic, the covering-up effects are the controlling factors; whereas in the case of dodecylamine, even though it is a smaller molecule, the effect on the soil's selective properties is more significant due to the hydrophobic property of dodecylamine.

5.3. Effects of Natural Organic Compounds on Ion-Exchange Reactions of Clay Minerals

The sources of the natural organic compounds used in this investigation were discussed in Section 3.1.2.2. The effects of these natural organic extracts on soil ion-exchange reactions were studied in a manner similar to that used with pure organic compounds. However, because an unknown composition and low concentrations were involved, no attempts were made to analyze these extracts. The effects of these extracts were examined in terms of the changes in the distribution of Sr^{++} ions on the basis of the total extracts added into the system.

The experimental results are presented in Figs. 44 and 45. The results show that the presence of these extracts in the system decreases

	Na ⁺	Sr ⁺⁺	Ca ⁺⁺	Clay Minerals, N
a,	0	2×10^{-4}	0	Sr-Mont.= 11.4×10^{-4}
b,	0	2×10^{-4}	6×10^{-4}	Na-Mont.= 5.4×10^{-4}
c,	5×10^{-3}	5×10^{-4}	0	Na-Mont.= 5.4×10^{-4}
d,	1×10^{-2}	1×10^{-4}	0	Na-Illite= 2.8×10^{-4}

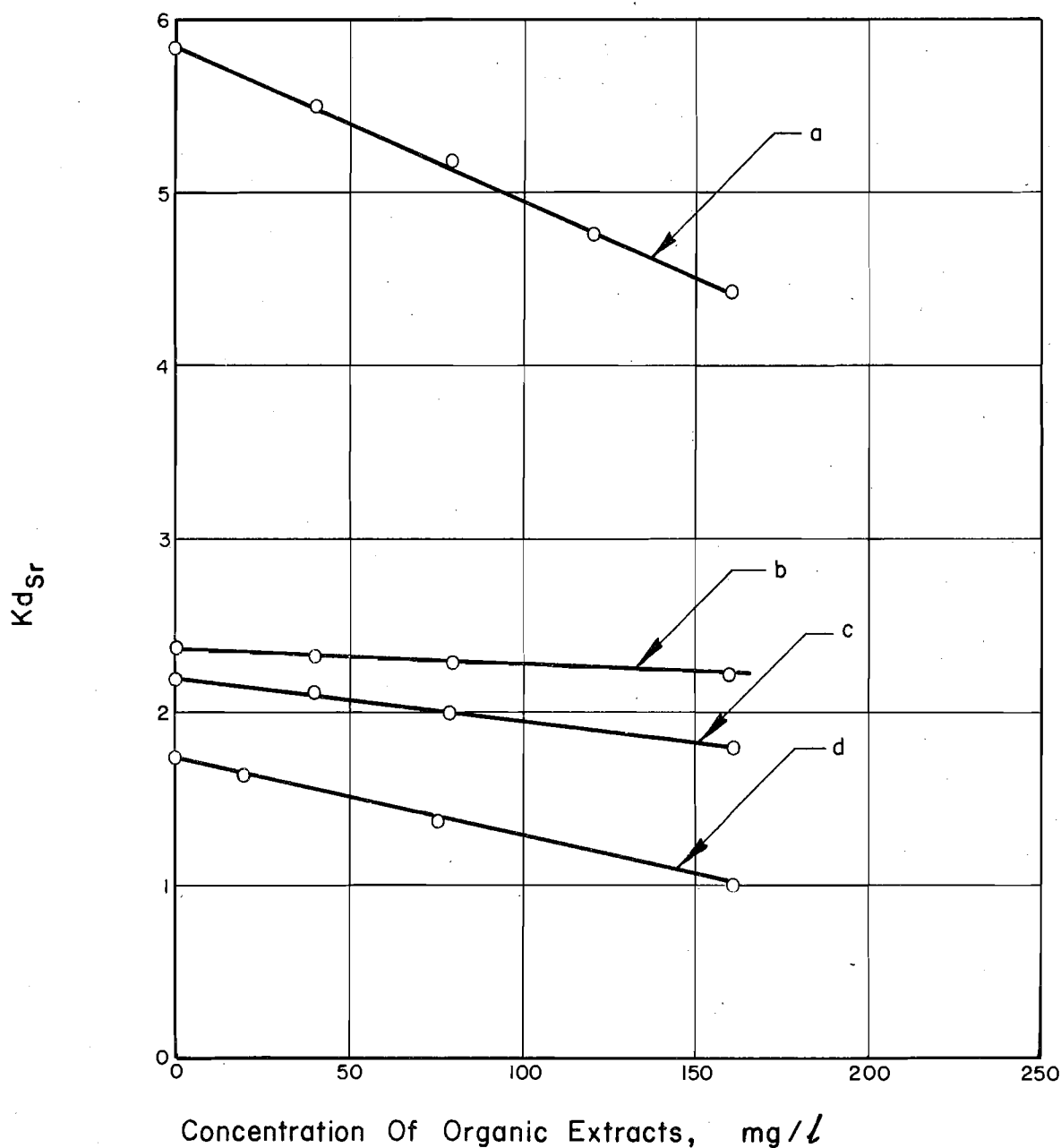


FIG. 44 EFFECTS OF SOIL ORGANIC EXTRACTS ON DISTRIBUTION OF COUNTER IONS.

	Sr^{++}	Counter Ions	Clay Minerals, N
a,	4×10^{-4}	$\text{Ca}^{++} = 4 \times 10^{-4}$	$\text{Na-Mont.} = 5.2 \times 10^{-4}$
b,	4×10^{-4}	$\text{Mg}^{++} = 4 \times 10^{-4}$	$\text{Na-Mont.} = 5.2 \times 10^{-4}$
c,	4×10^{-4}	$\text{Na}^+ = 6 \times 10^{-3}$	$\text{Na-Mont.} = 5.2 \times 10^{-4}$

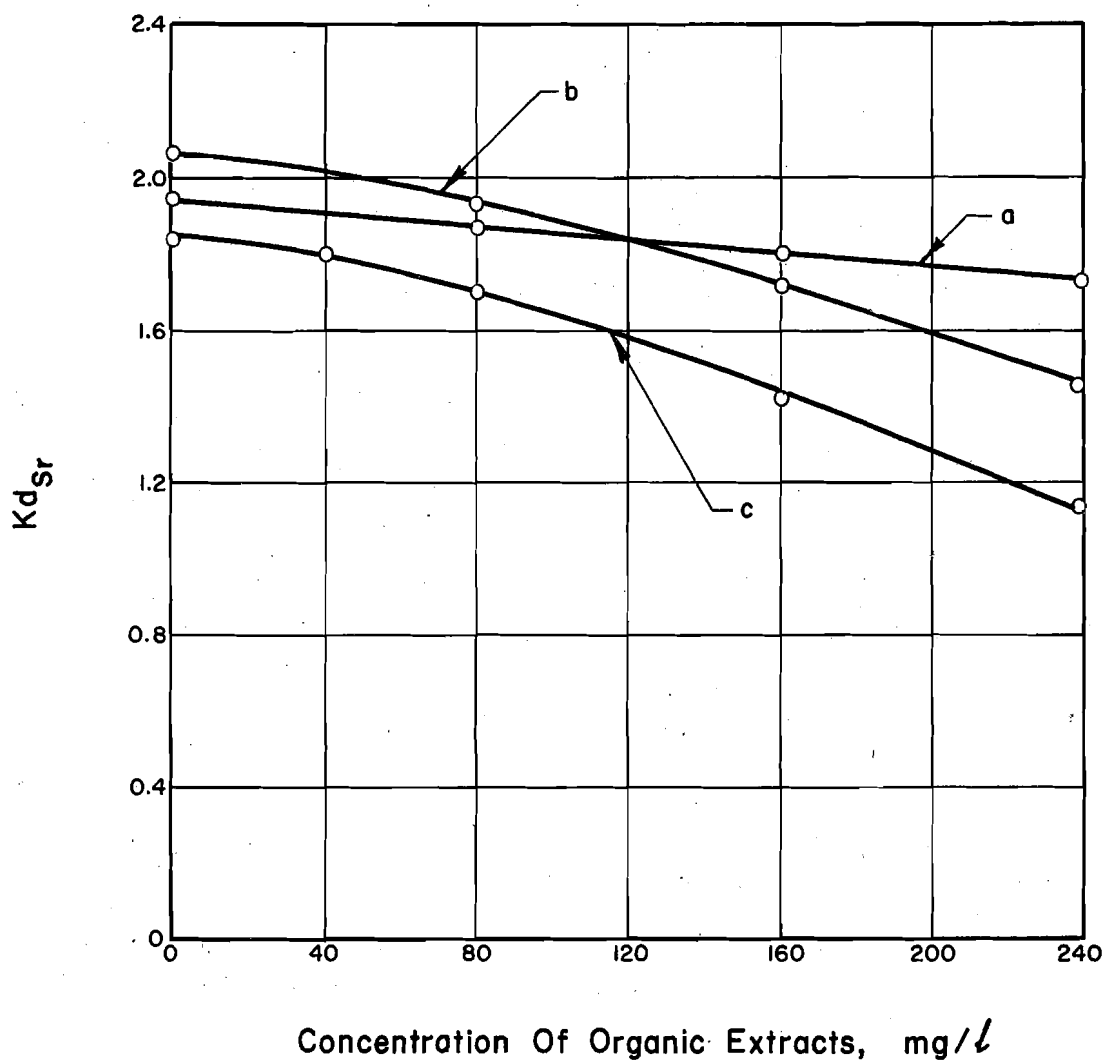


FIG. 45 EFFECTS OF GROUND WATER ORGANIC EXTRACTS ON DISTRIBUTION OF COUNTER IONS.

the effective distribution coefficients of Sr^{++} , $\overline{Kd}_{\text{Sr}}$. However, the degree of the effects was much less than for the pure organic compounds used. It is uncertain what factors affected the Sr^{++} distributions. Examination of the effects on the exchange reactions between the counter ion pairs $\text{Sr}^{++}\text{-Ca}^{++}$ (Fig. 45, curve a) and $\text{Sr}^{++}\text{-Mg}^{++}$ (Fig. 45, curve b) suggests that the effects may be due to weak sequestering agents.

As pointed out in Section 3.1.2.2., the extracts used in this investigation represent only a small fraction of the actual constituents of natural organics in the soil environment; and furthermore, because an inefficient extraction method was used, the organic compounds that may readily interact with soil materials were likely not included in the extracts. It is quite probable that the extracts may contain sodium salts of short chain organic acids.

6. SUMMARY AND CONCLUSIONS

Various ion-exchange expressions resulting from different forms of activity corrections have been subjected to experimental tests with montmorillonite and illite. The experimental results of the exchange reactions between Sr^{++} and several inorganic cations indicate that, except for the ion pairs involving hydrogen ions, all expressions, regardless of the differences in their values, have about the same degree of reliability in producing the constant values of the equilibrium constants.

On the basis of the experimental findings, it is concluded that the mass-action equilibrium expression without the activity corrections has the advantage of its simplicity, which allows the expression to be useful in predicting the equilibrium reactions of more complicated systems.

The constancy of the equilibrium constants of montmorillonite and illite for many inorganic counter ion pairs, exclusive of hydrogen ions, indicates that regardless of the differences in their causes, the relative selectivity of all the exchange sites in a clay mineral remain constant over a wide range of ion concentrations. The exceptional behavior of hydrogen ions is believed to be caused by the fact that the selectivity of each exchange site for hydrogen ions depends on the nature of each exchange site in a clay mineral.

Interactions of water-soluble, chelate-forming, organic compounds with counter ions and their effects on ion-exchange reactions were investigated using citrate, tartrate, and EDTA. The experimental results are compared with the effects predicted from the mass-action law of the ion exchange reactions and stability of the chelated compound. In general, the experimental results are in good agreement with the

qualitative rules of soil selectivities and the stabilities of the metal chelates. However, the exact quantitative prediction of the ion-exchange equilibrium in the presence of a sequestering agent was unsuccessful due to the fact that certain assumptions and approximations necessary for the prediction were invalid. The prediction of the ion-exchange equilibrium in the presence of sequestering agents was complicated by the fact that the stability of a chelated compound depended on the experimental condition, in addition to the fact that the sequestering agents also interacted with the soil exchange media.

The effects of sequestering agents on the distribution Sr^{++} ions depend on the nature and concentration of the competing counter ion present, and the mobility of Sr^{++} ion in soil is inversely proportional to $(1 + \overline{Kd})$. In the case of the counter ions, Ca^{++} and Zn^{++} , which form more stable chelates than does Sr^{++} , the presence of the sequestering agent increases the effective distribution coefficient of Sr^{++} , and this would decrease the rate of migration of Sr^{++} in the soil. On the other hand, when the competing counter ions are Mg^{++} and Na^+ , which form less stable chelates than does Sr^{++} , the presence of sequestering agents decreases the effective distribution coefficient of Sr^{++} , and would increase the rate of migration of Sr^{++} in the soil.

It is not probable that in a natural soil environment, the concentrations of natural sequestering agents are so high as to yield significant effects on the distribution of radionuclides disposed into the environment. Even for the waste released from a certain nuclear facility that may contain considerable amounts of sequestering agents, the presence of these sequestering agents may even be beneficial in

terms of delaying the movement of the hazardous radionuclides such as Sr^{90} and Cs^{137} , for the formation of stable chelated compounds of competing counter ions such as Ca^{++} and Al^{3+} may result in more favorable conditions for Sr^{90} and Cs^{137} to be adsorbed on the soil exchange media.

Adsorption of soil-sorptive organic compounds and its effects on the ion-exchange properties of clay minerals were investigated using methylamine, arginine, dodecylamine, and methylene blue. The effects of organic adsorption were examined in terms of the changes in the exchange capacities and the selective properties of clay minerals. On the basis of the experimental data, it is evident that certain organic cations such as dodecylamine and methylene blue are quite capable of reducing the exchange capacities and change the selective properties of clay minerals.

Large organic cations such as dodecylamine and methylene blue are so strongly adsorbed on clay mineral surfaces by Van der Waals forces, in addition to the coulombic forces, that the adsorption is practically irreversible. Because of this irreversible nature, the adsorption of these organic compounds resulted in the permanent reduction of the exchange capacities of the clay minerals. Theoretically, the adsorption of large organic compounds can result in complete annihilation of soil exchange capacities, if the organic compounds are available. However, in a natural environment, other factors such as microbial activities may control the organic concentrations in both solution and soil exchanger phases. Because of the complexity and unknown characteristics of natural organic compounds, it is impossible to make any prediction about the quantity of the reduction of the soil exchange capacities by natural organic compounds. To have a better accuracy in evaluation of ion-exchange reactions

of a natural soil, the effects of the presence of naturally occurring organic compounds in the exchange medium should be considered in the experimental determination of ion-exchange parameters of the medium.

The experimental results show that the adsorption of certain organic compounds can affect the soil exchange properties either by covering-up the exchange sites or by changing of a hydrophilic clay surface to a hydrophobic one.

The results of methylene blue adsorption indicate that methylene blue ions are capable of covering-up the exchange sites or trapping small inorganic cations on the clay mineral surfaces. The change of hydrophilic clay surfaces to hydrophobic surfaces by dodecylamine adsorption increases the selective properties of the clay minerals. The effects of the adsorbed organic compounds on the selective properties of clay minerals depend on the concentrations and sizes of the organic compounds. The effects increase as the size and concentration of the organic increase.

The effects of natural organic compounds on soil ion-exchange reactions were studied with organics extracted from ground water and surface soil materials. The degree of the effects of these extracts is much less than that of pure organic compounds. The experimental results suggest that the effects of these extracts may have been due to the presence of various sodium salts of short chain organic acids present in the extracts.

Considering all the probable effects of various organic compounds on soil ion-exchange reactions, it is apparent that for the accurate study of the distribution and transport of radionuclides disposed

into a soil environment, the involvement of organic constituents of the soil environment must be included.

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APPENDIX - SYMBOLS USED

a, b	Number of moles of counter ions
a_A, a_B	Activities of the cation A and B in the solution phase
\bar{a}_A, \bar{a}_B	Activities of the cation A and B in the exchanger phase
a_X, \bar{a}_X	Activities of anion X in the solution and exchanger phases
A^{a+}, B^{b+}	Cations
C_A, \bar{C}_A	Molar concentrations of the cation A in the solution and exchanger phases (moles/l)
C_v	Coefficient of Variation ($\frac{s.d.}{average} \times 100$)
cpm	Radioactivities (counter per minute)
C.E.C.	Cation Exchange Capacities (m.eq./100 grams or eq./l)
ΔG	Free energy change (Cal/mole)
I	Ionic strength (moles/l)
Kd_A, Kd_B	Distribution coefficients of the cation A and B
\bar{Kd}_A, \bar{Kd}_B	Effective distribution coefficients of the cation A and B
Ko_{AB}	Selectivity coefficients of exchanger for the cation A with respect to B
Ko_{AB}^i	Mass-action equilibrium constant with activity corrections
\bar{Ko}_{AB}	Effective equilibrium constant
K_{AB}^v	Vansellow's equilibrium constant
K_{AB}^k	Krishnamoorthy and Overstreet's equilibrium constant
Kth_{AB}	Thermodynamic equilibrium constants
m_A, m_B	Normal concentration of the cation A and B in the solution phase (eq./l)
\bar{m}_A, \bar{m}_B	Normal concentration of the cation A and B in the exchanger phase (eq./l)

m_A^O, m_B^O	Normal concentration of the cation A and B added to the system (eq./l)
m_Y	Normal concentration of the organic ligand Y^{y-} (eq./l)
γ_A, γ_B	Activity coefficients of the cation A and B in the solution phase
$\bar{\gamma}_A, \bar{\gamma}_B$	Activity coefficients of the cation A and B in the exchanger phase
γ_{AX}	Mean activity coefficients of the electrolyte AX in the solution phase
s.d.	Standard deviations
U_i, \bar{U}_i	Chemical potential of the cation I in the solution and exchanger phase (cal/mole)
v_A, v_B	Partial molar volumes of the cation A and B (liter/mole)
Y^{y-}	Organic ligands
z_a, z_b	Valences of the cation A and B

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